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VOLUME 6 No. 2/3

SEPTEMBER, 1954

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GEOCHIMICA ET COSMOCHIMICA ACTA

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VOLUME 6, NO. 2/3 SEPTEMBER 1954

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Isotopic composition of atmospheric oxygen and nitrogen*

Malcolm Dole, G. A. Lane, D. P. Rudd,
and D. A. Zaukelies

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(*Received* 26 *January* 1954)

ABSTRACT

High altitude air samples collected in glass bulbs during balloon flights up to heights of 87,000 ft were found to contain oxygen with a normal isotope ratio, deviations less than $\pm 0{\cdot}05\%$. Air samples collected in Aerobee rockets up to altitudes of 51·6 km contained nitrogen having a normal isotope ratio, deviations less than $\pm 0{\cdot}15\%$. The oxygen of the rocket samples contained a higher percentage of O^{18} than normal, but when an estimated correction was applied for the preferential loss of O^{16} by clean-up of oxygen by the steel collecting tanks, the O^{18} percentage of the oxygen in air at 51·6 km was normal to $\pm 0{\cdot}3\%$.

Air collected at ground level in a number of locations all over the world contained oxygen having a normal isotope ratio to $\pm 0{\cdot}025\%$. Air pumped out of ocean water at different depths in the Pacific Ocean contained oxygen having a higher O^{18} percentage than normal; the less the percentage of oxygen in the sample, the greater was the O^{18} percentage. The oxygen isotope fractionation factor for the process consuming dissolved oxygen was 0·991. The nitrogen isotope ratio in dissolved ocean air was normal.

The oxygen isotope fractionation factor for the clean-up or chemisorption of oxygen by steel was 1·026, while the factor was 1·061 for the clean-up of oxygen by copper.

Introduction

McQueen (1950) measured the N^{15}/N^{14} in nitrogen collected by rockets at altitudes between 41 and 58 km, and found separations of the nitrogen isotopes up to 3·9%. Hagelbarger, Loh, Neill, Nichols, and Wenzel (1951) pointed out, however, that on the basis of their studies and those of Chackett, Paneth, and Wilson (1949, 1950) and Chackett, Paneth, Reasbeck, and Wiborg (1951) of the argon to nitrogen and helium to nitrogen ratios, which showed no evidence for the gravitational separation of the components of the atmosphere at altitudes up to 60 km, it was extremely unlikely that the observations of McQueen represented a real effect. In this paper a study similar to that of McQueen has been carried out using more refined techniques.

Gravitational equilibrium (at constant temperature) would produce a decrease in the O^{18}/O^{16} ratio with height over ranges of altitude where such an equilibrium existed. Roake and Dole (1950) concluded that in the case of oxygen a reverse effect might exist, that is, an increase of the O^{18}/O^{16} ratio with altitude. The basis of their argument was the fact that the photosynthesis reaction in the oceans is producing oxygen whose O^{18}/O^{16} is smaller than that of ground level oxygen by the factor 0·983. (For a review of these facts as well as other information related to the oxygen isotopes, see M. Dole (1952).) This means that elsewhere in the world there must exist a process or processes in which the O^{18}/O^{16} ratio is being enhanced. Such a process might be the irreversible and random exchange

* This research was supported by the Air Force Cambridge Research Center and by a grant from the Abbott Research Fund of Northwestern University.

of oxygen isotopes between molecular oxygen and carbon dioxide as promoted by the intense ultraviolet light of the sun in the stratosphere,

$$CO^{16}O^{18} + O_2{}^{16} \rightarrow O^{16}O^{18} + CO_2{}^{16} \qquad (1)$$

Carbon dioxide in equilibrium with liquid (fresh) water at 0°C is known to contain oxygen having a greater O^{18}/O^{16} ratio than that of air by the factor 1·015 (DOLE, 1952; UREY, 1947). If carbon dioxide which has equilibrated with water, diffuses

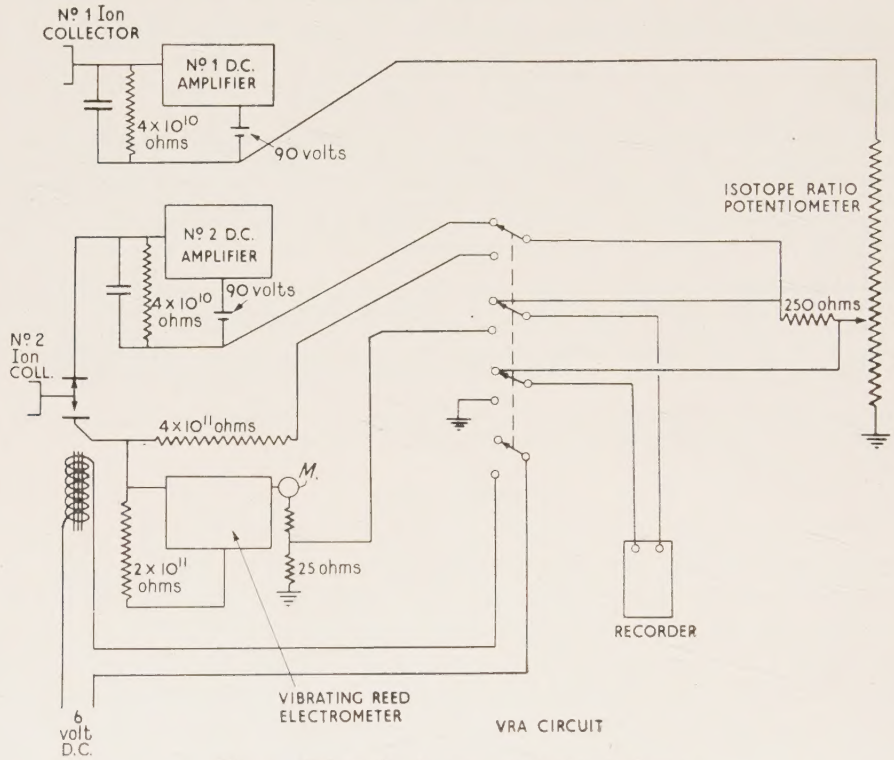

Fig. 1. Schematic diagram of electrical circuit.

or is carried by convection to the upper atmosphere where reaction (1) can occur, it might be expected that the O^{18}/O^{16} ratio of stratospheric oxygen would be slightly greater than that of ground level oxygen. If the air is mixed rapidly by vertical components of winds, an enhanced O^{18}/O^{16} ratio in the upper atmosphere could not be observed. It was the purpose of this research to investigate the various possibilities mentioned above. In so doing improved mass spectrometric techniques for relative isotope abundance measurements had to be adopted and sources of error eliminated, in particular the error due to fractionation of the oxygen isotopes during the clean-up or chemisorption of oxygen by metal surfaces.

EXPERIMENTAL

1. *The electrical system*

A Consolidated Engineering Corporation Nier isotope-ratio mass spectrometer, whose normal operating reproducibility is a few tenths of a per cent, was modified

electrically by the introduction of a General Electric Co. recording photoelectric potentiometer, an Applied Physics Corporation vibrating reed electrometer, and an electronic voltage stabilizer, type IE5101 of the Superior Electric Company. The 4×10^{10} ohm input resistor was replaced by a 4×10^{11} ohm resistor when

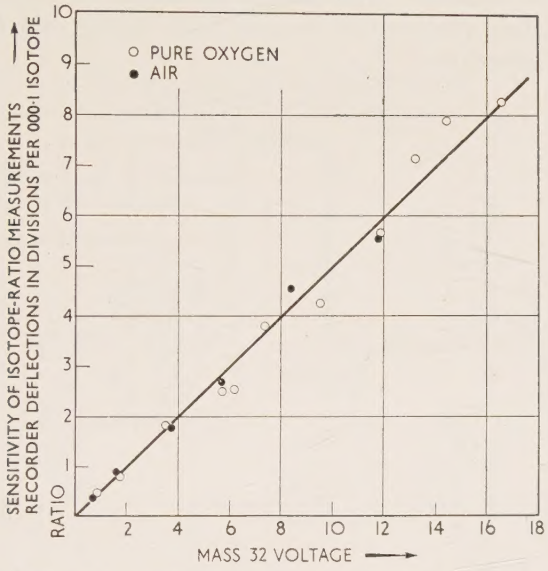

Fig. 2. Sensitivity of the mass spectrometer in terms of divisions deflection of the recorder pen per 0·1% change of the voltage ratio of mass 34 to mass 32.

using the vibrating reed amplifier. This increased 10-fold the magnitude of the measured voltage ratio. A polyethylene supported switch was built into the desiccated electrometer tube chamber so that the electrical input from the plate

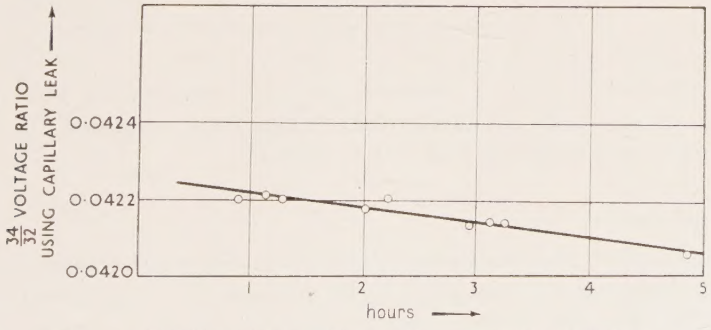

Fig. 3. Stability of the voltage ratio as a function of time.

receiving the ion beam of greater mass (the No. 2 collector) could be switched either to the vibrating reed or to the electrometer tube of the regular amplifying circuit of the mass spectrometer. The parts of the switch external to the desiccated chamber had to be shielded. Fig. 1 is a schematic diagram of the electrical circuit. The sensitivity of the electrical measuring equipment in terms of divisions deflection

of the recorder per 0·1% change of the voltage ratio of mass 34 to mass 32 is illustrated in Fig. 2 as a function of the mass 32 voltage on the No. 1 collector. Many samples of air having oxygen percentages lower than 20·9% (the normal value for air) were studied with the mass spectrometer. It is obvious from Fig. 2, that the lower the percentage of oxygen in the sample, the lower the sensitivity for the same input pressure. The sensitivity could be increased somewhat by increasing the manifold pressure of the gas under study, but there were practical limits to the input pressure.

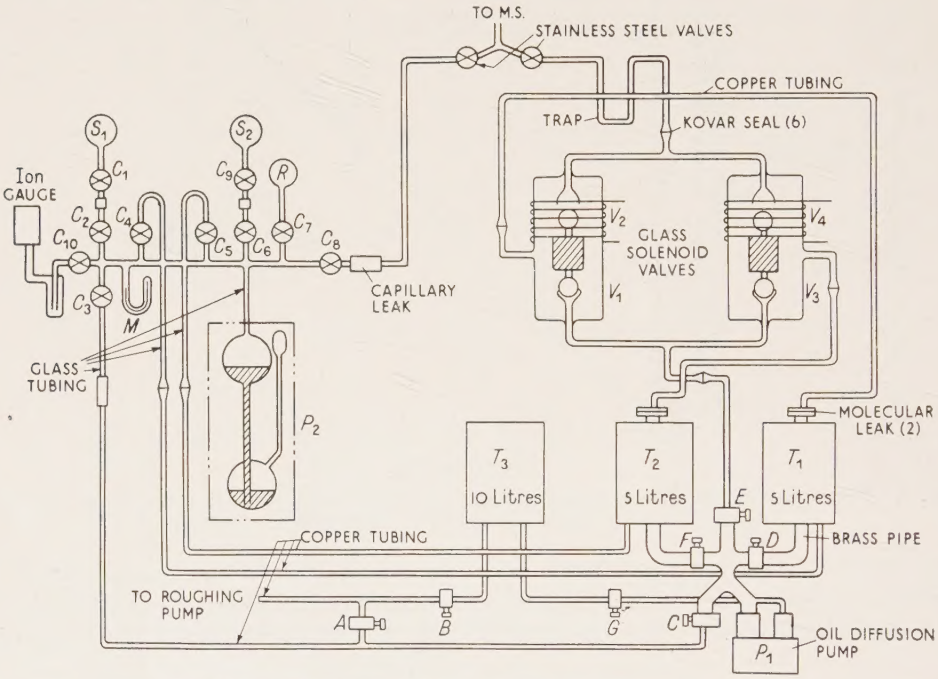

Fig. 4. Vacuum system of the mass spectrometer.

The data plotted in Fig. 3 demonstrate the stability of the voltage ratio measurements of the mass spectrometer. They were obtained on a sample of pure oxygen using the capillary leak input system.

2. *The vacuum system*

The modified manifold and vacuum system of the mass spectrometer is illustrated in Fig. 4. By means of stainless steel Hoke vacuum valves gas could be admitted to the ionization chamber of the mass spectrometer either through the capillary leak supplied with the instrument or through a pin-hole leak system built into the instrument.

The scheme of MCKINNEY, MCCREA, EPSTEIN, ALLEN, and UREY (1950) of comparing an unknown gas sample with a sample of known isotopic composition in the period of a few minutes by first introducing the known gas into the mass spectrometer and then the unknown gas was adopted. The standard and unknown

samples of gas were separately measured out in a 25 cc bulb at a predetermined pressure and then expanded into one of two 5-litre brass tanks. A solenoid operated ball joint glass valve system permitted the operator to allow each sample to flow either into the mass spectrometer or to waste. There was an annoying large

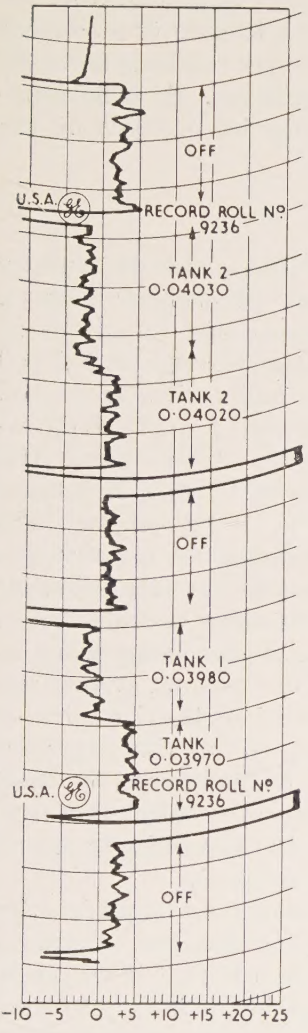

Fig. 5. A typical record of the mass spectrometer performance.

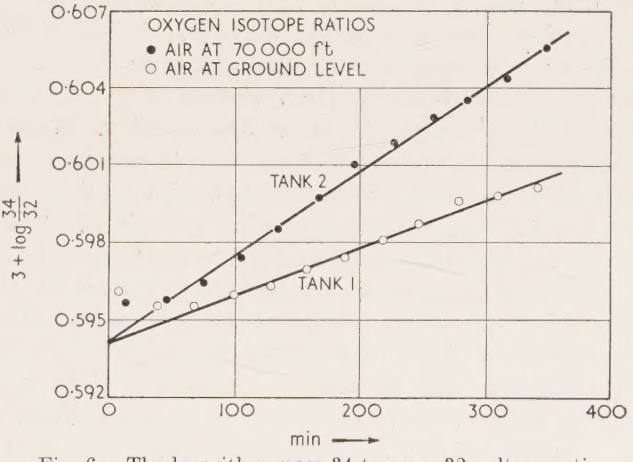

Fig. 6. The logarithm mass 34 to mass 32 voltage ratio as a function of time.

shift in the measured voltage ratio during the one minute period of changing over from one of the gas samples to another. As a result, it was the custom of the operator to record the zero trace of the amplifier during the change-over period. A typical record is shown in Fig. 5.

A variation of isotope ratio with input manifold pressure as noted by HALSTED and NIER (1950) was also observed by us. Because of the fact that molecular flow occurred through the pin-hole leaks, the lighter isotopic species diffused at a more rapid rate through the molecular leaks than the heavier. As a consequence the 34/32 ratio of the oxygen isotopes remaining in the tanks increased with time.

The logarithm of the observed voltage ratio should be a linear function of the time. This theoretical expectation was fully realized as is demonstrated by the data of Fig. 6 where the mass 34 to mass 32 voltage ratio obtained on a sample of air collected at 70,000 ft is compared with the voltage ratios for a sample of ground level air. The straight lines represent a least squares equation calculated from the measured voltage ratios. By extrapolating the lines back to zero time, a very accurate measure of the voltage ratio was obtained and errors resulting from the initial influx of gas into the mass spectrometer were eliminated. Such measurements on a single sample lasted several hours and were carried out only on the most important samples.

3. *Corrections for mass* 34 *impurities*

The sensitivity of the relative 34/32 voltage ratio was such that a mass 34 impurity of 6×10^{-5} mm partial pressure in a sample of air at atmospheric pressure could have been detected. For this reason it was essential that impurities be rigidly excluded. In this research all air samples were passed through an 8-ft coil of glass tubing immersed in liquid air. Experiments with radioactive tracers had previously shown that such a long length of tubing was required (Calvin, Heidelberger, Reid, Tolbert, and Yankwich, 1949, p. 133). After taking this precaution there was no significant variation of the mass 34 to mass 32 voltage ratio with composition of the gas over the range 100% to 2% oxygen. The constancy of this ratio with variation in the percentage composition is a stringent test of the absence of a mass 34 impurity. However, before the measurements on the rocket samples had been completed, the mass spectrometer vacuum system became accidentally contaminated with oil from the oil diffusion pump when its condensing water stopped flowing overnight. Although the vacuum system was cleaned as well as possible and a new analyzer tube obtained from the Consolidated Engineering Corporation, an impurity of mass 34 from then on was always present during isotope ratio measurements. Its magnitude could be determined by direct measurement of the mass 34 voltage on the No. 2 collector or by calculation from the observed mass 34 to 32 voltage for 20% oxygen and the theoretically correct voltage ratio (as estimated from measurements on 100% oxygen).

The data of Fig. 7 demonstrate that the mass 34 impurity was a linear function of the pressure (in this case of nitrogen gas) in the analyzer chamber. Assuming that the mass 34 impurity depended only on the pressure and that it was independent of the composition of the sample under investigation, it is easy to show that the measured mass 34 to mass 32 voltage ratio, r, should be related to the true ratio, r_0, and the percentage of oxygen in the sample, C, by the equation

$$r = r_0 + k/C \tag{2}$$

This relationship is illustrated in Fig. 8 where r is plotted as a function of $1/C$. Three separate series of measurements over a period of a year gave 0·0107, 0·0122 and 0·0116 for the constant k of Eq. (2). Thus there was no significant alteration in the magnitude of the mass 34 impurity in a year of constant evacuation of the vacuum system. By means of Eq. (2) all voltage ratio measurements on both

standard and unknown samples were corrected for the mass 34 impurity. The percentage of O^{18} in the sample was then calculated using the equation

$$\%O^{18} = 0{\cdot}2039 \times \frac{\text{voltage ratio unknown}}{\text{voltage ratio standard air}} \qquad (3)$$

The value of $0{\cdot}2039\%O^{18}$ adopted for the oxygen of air is the value given by NIER (1950).

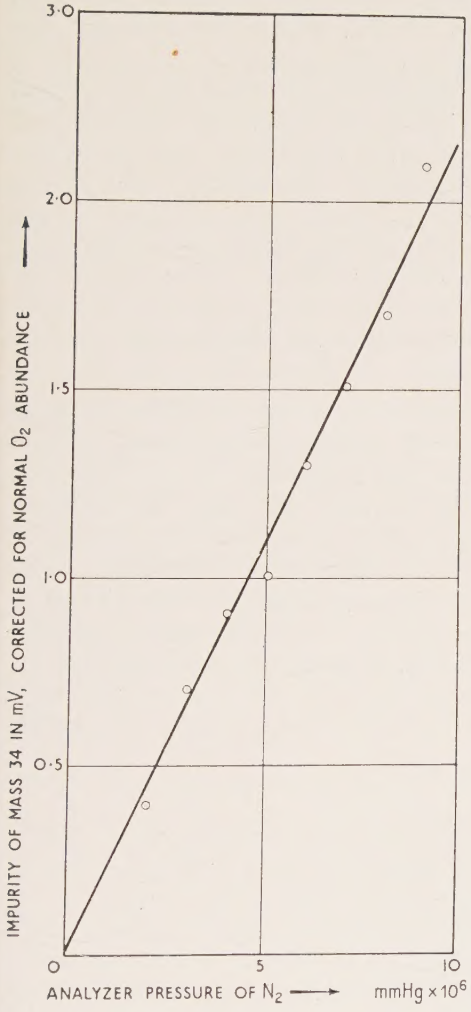

Fig. 7. Mass 34 impurity as a function of the pressure in the analyzer chamber.

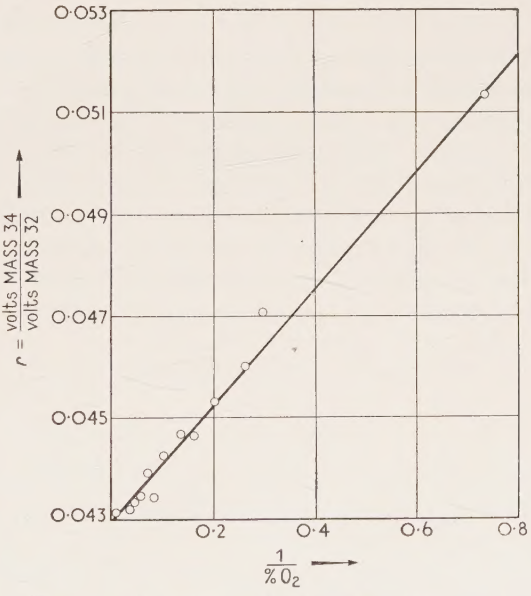

Fig. 8. Mass 34 to mass 32 voltage ratio as a function of the reciprocal of the oxygen %.

4. *Source of air samples*

To obtain air samples from different geographical locations at ground level evacuated glass tubes with capillary tips were mailed to scientists in different parts of the world. The tips were broken open and resealed after the air filled the tube. The tubes were then returned to Evanston. Samples of air pumped out of ocean water taken from different depths in the Pacific Ocean were obtained

from the Scripps Institution of Oceanography, La Jolla, California, through the co-operation of Dr. Norris M. Rakestraw. Samples of photosynthetic oxygen from the Pacific Ocean were collected by spreading a 100-sq ft polyethylene sheet about 2 in. under the surface of the water over a kelp bed near San Diego.

Air samples up to 87,000 ft were collected during balloon flights at the Holloman Air Development Center, New Mexico. An apparatus containing two 230 cc glass bulbs with a special vacuum stopcock was constructed, the glass bulbs evacuated and the equipment sent to Holloman. After the stopcocks had been automatically opened and closed during the balloon flight, the sampler was parachuted to earth and the glass bulbs returned to Evanston.

Two air samples obtained during rocket flights were donated by the Signal Corps Project No. 172B at the Engineering Research Institute, University of Michigan. These air samples were collected in large evacuated steel cylinders. During the collection the steel surface chemisorbed or "cleaned-up" part of the oxygen so that it became necessary to determine the extent of fractionation of the oxygen isotopes on chemisorption by metal surfaces. The next section describes the results of this work.

Oxygen Isotope Effects on Chemisorption of Oxygen by Metal Surfaces

The fractionation factor for chemisorption of oxygen isotopes on metal surfaces at room temperature was determined by exposing oxygen gas at about 100 mm pressure to a large surface of the metal which had previously been reduced in hydrogen, and after about 10 or 25% of the oxygen had been chemisorbed, measuring the isotope ratio of the remaining gas. If w_g represents the fraction of oxygen unreacted after time t, w_m the fraction of oxygen chemisorbed, y_0, y_g and y_m, the percentages of O^{18} in the initial gas, in the gas phase after time t and in the oxygen chemisorbed on the metal, respectively, and x_0, x_g and x_m similar percentages for the isotope of mass 16, then material balance requires that

$$w_g + w_m = 1 \tag{3}$$

$$x_0 = w_g x_g + w_m x_m \tag{4}$$

$$y_0 = w_g y_g + w_m y_m \tag{5}$$

Defining the fractionation factor α by the expression

$$\alpha = y_g x_m / y_m x_g \tag{6}$$

it is easy to show that

$$\alpha = \frac{y_g - w_g y_g}{y_0 - w_g y_g} \tag{7}$$

for the case that x_0/x_g approximately equals unity which was amply true in this research.

By measuring the initial O^{18} percentage in the gas before chemisorption, y_0, and the percentage of $O^{18} y_g$ after the fraction $(1 - w_g)$ of the oxygen had been removed from the gas phase by chemisorption, α was readily determined by (7). Knowing α, w_g and y_g in the air samples collected in the steel tanks during the

rocket flights, y_0, which should be the percentage of O^{18} in the air sample before the clean-up of any of its oxygen, was calculated from the equation

$$y_0 = \frac{y_g}{\alpha}\,[1 + w_g(\alpha - 1)] \tag{8}$$

Experiments showed that α for chemisorption of oxygen at room temperature on steel was 1·026 and on copper 1·061. There seemed to be no variation of α with the extent of oxidation. The temperature dependence of α has not yet been studied.

The details and further discussion of oxygen isotope effects on chemisorption by metals will be submitted for publication elsewhere.

Percentage of O^{18} in Air Samples Taken from Different Geographical Locations

A great number of measurements of the percentage of O^{18} relative to Evanston air were made on air samples collected from many different parts of the world. Inasmuch as the results showed no significant deviations from the percentage of O^{18} in Evanston air, the data will not be tabulated here. The relative error was as low as 0·025% of 0·2039%O^{18} in the best measurements. When deviations greater than this were obtained, repetitive experiments done by the method illustrated in Fig. 6 reduced the deviations to $\pm$0·025%. Air samples were obtained from the ONR Arctic Research Laboratory at Point Barrow, Alaska, from an ice island at 88° 16′ N and 89° 30′ W, from Greenland, Finland, Holland, Panama City, Panama, Lima and Huancayo, Perú, Santiago and Concepción, Chile, Buenos Aires, Argentina, Sao Paulo, Brazil, Melbourne, Australia, Tokyo, Japan, from 8° S, 115° W over the Pacific Ocean, and from a number of locations within the United States. All samples were constant in the respect to their isotopic composition of O^{18}. This agrees with the finding of Glückauf and Paneth (1946) who analyzed air for its helium content at many different locations. They could detect no variations in the relative abundance of helium at ground level.

Percentage of O^{18} in Air from the Pacific Ocean

Ocean water saturated with air at atmospheric pressure dissolves relatively more oxygen than it does nitrogen so that the percentage of oxygen in dissolved ocean air is approximately 33% as compared to 20·9% in the atmosphere. Near the surface of the ocean, photosynthesis by plankton, kelp or other green salt water plants maintains the water saturated with oxygen, but at lower levels where the sunlight intensity is reduced practically to zero, the percentage of oxygen falls to values as low as 2%. At still lower depths the percentage of oxygen in the dissolved air rises. It was expected that photosynthesis which can be shown (Dole, 1952) in the laboratory to produce oxygen having a lower O^{18}/O^{16} ratio than atmospheric oxygen by the factor 0·983 would cause the dissolved ocean air to contain a smaller percentage of O^{18} than normal air. However, as the oxygen is removed from the water by the action of bacteria, plankton and sea-life (in photochemical terms by a back thermal reaction) it was expected that the residual oxygen remaining in

the water would contain a larger than normal percentage of O^{18}. Both of these expectations were realized.

A mathematical relationship between the percentage of $O^{18} y_w$, in the air dissolved in the ocean water and the percentage of oxygen, c, in the air at the depth h can be derived in the following way. Consider a litre of ocean water at depth h containing oxygen at concentration c with a percentage of O^{18} equal to

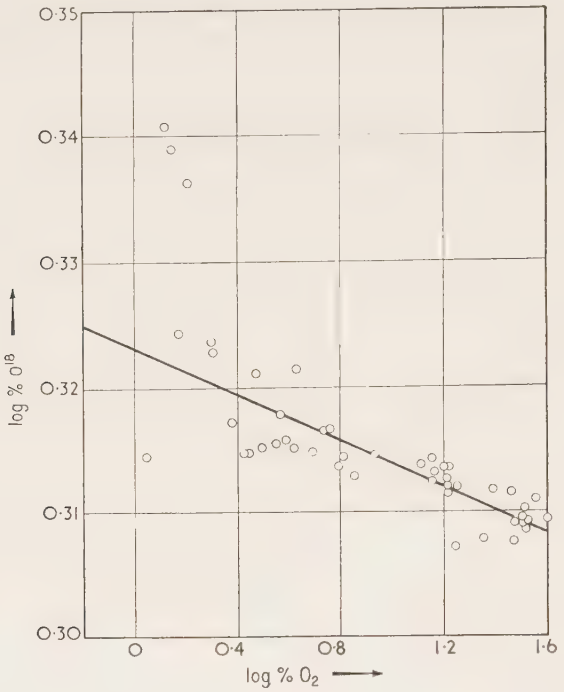

Fig. 9. A test of equation (11).

y_w. Let it be transferred to a depth $h + dh$ at a concentration $c + dc$ and an O^{18} percentage $y_w + dy_w$. For material balance it is necessary that

$$cy_w = (c + dc)(y_w + dy_w) + y_B\, dc_B \tag{9}$$

where y_B is the percentage of O^{18} in the oxygen of amount per litre, dc_B, consumed by bacteria, plankton, etc. Letting the fractionation factor α equal y_B/y_w, Eq. (9) may be rearranged to

$$(\alpha - 1)\frac{dc}{c} = \frac{dy_w}{y_w} \tag{10}$$

inasmuch as $-dc_B$ equals dc.

Integrating between limits assuming α to be independent of the extent of oxygen removal, Eq. (10) becomes

$$(\alpha - 1)\ln\frac{c_2}{c_1} = \ln\frac{y_{w,2}}{y_{w,1}} \tag{11}$$

In Fig. 9 a plot of log $\%O_2$ versus log y_w is given. From the slope of the straight line, α was estimated to be 0·991. The data scatter considerably due to the difficulty of making accurate O^{18} percentage measurements in samples of air containing small percentages of oxygen. The data of Fig. 9 represent air collected down to depths of 2500 metres at four different locations in the Pacific Ocean. As

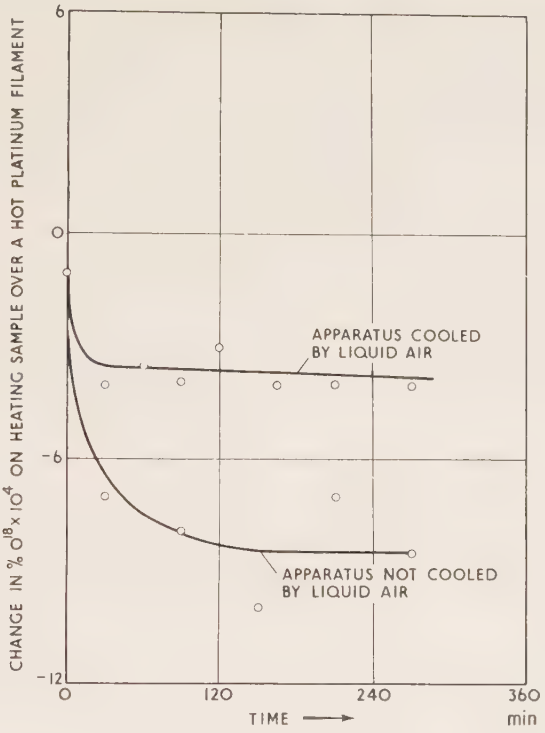

Fig. 10. Decrease in the mass 34 to 32 voltage ratio due to exchange of oxygen with water vapour on a hot platinum filament.

far as can be estimated from the rather uncertain data no significant difference exists between the results from the four different locations. The first series of data was obtained before a correction for the impurity of mass 34 was necessary.

The second series of measurements was carried out on air which had been passed over a hot platinum filament to burn out impurities. This turned out to be unnecessary inasmuch as the data were unchanged when the heat treatment was properly carried out. The heat of the filament was sufficient, apparently, to drive water off the inner glass surface of the combustion tube, unless the glass walls were cooled in liquid air. On the hot platinum filament the oxygen of the water readily exchanged with molecular oxygen causing a reduction of the percentage of O^{18} in the air. The results showing this effect are given in Fig. 10.

No variation of the N^{15}/N^{14} ratio with depth could be detected. The amount of nitrogen dissolved in the ocean remains practically constant with depth.

Isotopic Composition of High Altitude Oxygen and Nitrogen

Data obtained on the high altitude samples are given in Table 1 along with three comparisons of ground level air with ground level air so that the order of reproducibility of the results can be judged. The data were obtained by the extrapolation technique illustrated in Fig. 6. No significant change of the N^{15}/N^{14} ratio with altitude up to 51·6 km is evident, nor was any change of the O^{18}/O^{16} ratios detected in the case of the air samples collected during the balloon flights. But a large and significant increase in the O^{18}/O^{16} ratio is seen to have been measured on the samples collected by rockets. However, to the latter data two corrections must be applied; first, a correction for the fact that the percentage of oxygen in the rocket samples was less than that of ground level air and, second, a correction for the fractionation of oxygen isotopes due to chemisorption on the steel walls of the collecting tank. Table 2 contains the data for the first correction as calculated using Eq. (2), and Table 3 the data for the second correction as calculated using Eq. (8).

Table 1. *Oxygen and nitrogen isotope voltage ratios for high altitude air*

Altitude metres	*Means of collection*	*Date measured* Da	Mo	Yr	*Mass* 34 *to mass* 32 *voltage ratio* Sample	Standard air	*Difference* %
Ground level		27	6	52	0·03944	0·03942	$+0·0_5$
21,300	Balloon	1	7	52	0·03928	0·03927	$+0·0_{25}$
Ground level		2	7	52	0·03929	0·03924	$+0·1_2$
Ground level		26	9	52	0·03991	0·03991	0
25,600	Balloon	27	9	52	0·03983	0·03984	$-0·0_{25}$
26,500	Balloon	31	10	52	0·04222	0·04224	$-0·0_5$
26,500	Balloon	4	11	52	0·04224	0·04225	$-0·0_{25}$
46,400	Rocket	1	8	52	0·03993	0·03942	$+1·2_7$
46,400	Rocket	12	8	52	0·04012	0·03979	$+0·8_2$*
51,600	Rocket	4	9	52	0·03981	0·03954	$+0·6_8$
					Mass 29 *to mass* 28 *voltage ratio*		
46,400	Rocket	31	7	52	0·07063	0·07062	$-0·0_1$
46,400	Rocket	25	8	52	0·07033	0·07062	$-0·4_1$†
46,400	Rocket	26	8	52	0·07021	0·07023	$-0·0_3$†
51,600	Rocket	3	9	52	0·06998	0·07010	$-0·1_7$

* Measured against a standard containing 17·2% O_2 and 82·8% N_2.
† Sample passed over a hot platinum filament before measurement.

The three measurements on the two rocket samples agree very well and average 0·2045%O^{18} after applying both corrections. This value is slightly higher by 0·3% than the percentage of O^{18} in ground level air, but considering the fact that the applied corrections were considerably greater than the 0·3% difference, the latter can hardly be considered to be significant. For example, if the fractionation factor for chemisorption were raised to 1·040, the y_0 values of Table 3

would be lowered to 0·2039%. Inasmuch as the collecting tank contained a copper inlet tube which could have chemisorbed some of the oxygen, a value of the fractionation factor equal to 1·040 does not seem unreasonable. There is the problem also of knowing the temperature of collection and the exact fractionation factor existing at that temperature.

Table 2. Corrections to the oxygen isotope voltage ratios of the rocket samples due to the mass 34 impurity

Sample	$\%O_2$	*Correction to voltage ratio*	*Corrected voltage ratio*	$\%O^{18}$
Air	20·9	−0·00051	0·03891	0·2039
46,400 m	16·2	−0·00066	0·03927	0·2058
O_2-N_2 mixture	17·2	−0·00062	0·03917	0·2043
46,400 m	16·2	−0·00066	0·03946	0·2058
Air	20·9	−0·00051	0·03903	0·2039
51,600 m	18·0	−0·00059	0·03922	0·2050

Table 3. Corrections to the $\%O^{18}$ of the rocket samples due to chemisorption on collection

Sample	$\%O^{18}$ *in sample after collection* y_g	w_g	α	$\%O^{18}$ *in sample before collection* y_0
46,400 m	0·2058	0·775	1·026	0·2046
46,400 m	0·2058	0·775	1·026	0·2046
51,600 m	0·2050	0·861	1·026	0·2043
				Ave. 0·2045

Conclusions

At the present time the data indicate no significant variation in either the oxygen or nitrogen isotope ratios with height. Thus, no positive proof of the explanation of the "Dole Effect," or the enhanced O^{18}/O^{16} ratio of atmospheric oxygen over that of the oxygen in water (or over that of photosynthetic oxygen), in terms of the mechanism involving the exchange of oxygen isotopes between carbon dioxide and oxygen in the stratosphere has been obtained.

Another possible explanation of the Dole effect is that the back thermal reaction of photosynthesis or any process removing oxygen from the atmosphere produces a fractionation of the oxygen isotopes by removing O^{16} at a greater rate than O^{18}. For the removal of oxygen in the ocean, the fractionation factor for this process was found above to be 0·991. This is not quite large enough as the factor should be 0·2005/0·2039 or 0·983. The value 0·2005 is the estimated (Dole, 1952) percentage of O^{18} being produced by photosynthesis in the oceans.

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The use of zone theory in problems of sulphide mineralogy

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ABSTRACT

The metallic or semi-metallic characteristics of many sulphide minerals, demonstrated by such properties as ductility, metallic lustre and low electrical resistivity are evidence of the metallic nature of their chemical bonds. This justifies a limited application of the electronic theories of the metallic state to problems involving these minerals.

The important Brillouin zones of some of the minerals in the iron-copper-sulphur system have been determined. The volumes of these zones, and the electron-to-atom ratios required to fill them, have been calculated. These minerals exhibit the properties of intrinsic semi-conductors and therefore it is assumed that free electron states exactly fill one of the zones, with an energy gap between the filled zone and the next higher zone. In the field from digenite to chalcopyrite the structural type is maintained, despite the increase in the iron to copper ratio, by the omission of sufficient metal atoms to avoid increasing the electron-to-atom ratio beyond the capacity of the filled zone. The existence of two structurally different types of sulphur in covellite and possibly in chalcocite is used to explain the apparent discrepancy between the zone capacity and the electron-to-atom ratio of these minerals.

Introduction

The metallic or semi-metallic nature of many sulphide minerals, demonstrated by such properties as low electrical resistivity, ductility, and metallic lustre, has long been known to mineralogists. However, in attempting to solve crystal chemical problems involving the sulphides, the common approach has been through the covalent nature of their bonds. Often much attention is given to the partial ionic character of the bonds but very little, if any, is given to the possible metallic nature. In a recent contribution, Ahrens (1953) showed a relationship between ionization potential of the various metals and some general structural features of their sulphides. However, this approach does not as yet seem to show promise of explaining such problems as the non-stoichiometric nature of many sulphides, the shapes of the solid solubility fields, and the location of the phase boundaries in sulphide phase diagrams. In these respects the sulphides seem to resemble intermetallic phases.

Much progress has been made over the past decade in the development of theories of metallic state. Recently Hume-Rothery (1946, 1948) has written several excellent books that contain lucid explanations of the semi-quantitative aspects of these theories. A thorough understanding of the more exact details requires a knowledge of mathematical physics but, as many approximations are necessary to facilitate these solutions, little information or new ideas are added to improve upon the semi-quantitative approach.

Solid Solubility

The problems of the non-stoichiometric nature of many sulphides and the location of phase boundaries in sulphide systems mentioned above are closely analogous to those of intermetallic compounds. These problems may be conveniently reduced to one of solid solubility, for the non-stoichiometric compounds can be looked upon as compounds in which one of the following occurs:

1. An excess number of atoms of one constituent are in sites normally occupied by another constituent. (Substitution solid solution.)

2. An excess number of atoms of one constituent are in holes or interstitial openings in the structure. (Addition or interstitial solid solution.)

3. A number of atoms of one constituent are missing (defect structure or subtraction solid solution). One can look at this type as the substitution of a hole for an atom, as in pyrrhotite, for example.

Consequently, the deviation from a Daltonide compound of strict stoichiometric ratio may be looked upon as the measure of degree of solid solution. An important factor that controls the extent of substitution in solid solutions, regardless of the type of bonding, is the relative size of the atoms or ions. A 15% difference in size is considered the maximum difference two ions or atoms can have and still exhibit appreciable solid solubility (Hume-Rothery, Mabbot, and Channel-Evans, 1934). With smaller differences in size, mutual solubility might be expected, providing other factors are favourable. The next most important factor is the electrochemical difference. A convenient measure of this, in principally ionic compounds, has been shown to be the ionization potential (Ahrens, 1953). An appreciable difference in ionization potential between the substituting and substituted atoms would be a deterrent to much mutual solubility.

Where the principal bonding in the crystal can be considered covalent, as perhaps it has been in the sulphides, factors involving the structures of the individual atoms seem to play a more important role. The large difference in ionization potential between iron and copper has been advanced as the reason for the low solubility of copper in pyrrhotite (FeS) (Ahrens, 1953). This should also mean that there would be low solubility of iron in the copper sulphide minerals, which has been shown by Merwin and Lombard (1937) not to be the case. A single phase field extends from the mineral digenite (Cu_5S_9) all the way past bornite (Cu_5FeS_4) (Schlegel and Schuller, 1952). At least two ordered phases appear in this field (Tunell and Adams, 1949; Frueh, 1950). An explanation more consistent with the directional properties of covalent bonding is as follows. Various bonding configurations exist in stable copper compounds of covalent nature. In cuprite (Cu_2O) the copper atoms are in 2-co-ordination and utilize hybrid sp orbitals. Copper forms tetrahedral sp^3 bonds in chalcopyrite ($CuFeS_2$) and cubanite ($CuFe_2S_3$) and 4-planar dsp^2 bonds in tenorite (CuO). No structure has been described where copper forms octahedral d^2sp^3 bonds.* In pyrrhotite and in pyrite (FeS_2) iron occupies an octahedral position utilizing d^2sp^3 bonds; consequently, copper could not be expected to be very stable as a substitute for iron in these structures. On the other hand, iron, being a transition metal, is capable of great flexibility in the use of its bonding orbitals, and in some structures, such as chalcopyrite and cubanite, it is quite content to form tetrahedral sp^3 bonds; therefore we can expect it to substitute for tetrahedrally bonded copper to a considerable extent.

This same argument should apply equally well to covellite, as one of the two structurally distinct copper positions in this mineral is similar to that of copper

* In murdochite, a new mineral with the formula Cu_6PbO_8, the copper (Cu^{++}) is octahedrally co-ordinated. See J. Phys. Chem., **21**, 1897, 1953. (Ed.)

and iron in chalcopyrite. However, we notice in Fig. 1 that there seems to be little, if any, solubility of iron in covellite or in chalcocite. (The structure of the latter mineral has not been determined.) Therefore it might be well to consider additional factors that might effect solid solubility.

In intermetallic phases, when both the size factor and electrochemical factor appear to favour solid solubility, there is another factor that determines limit of solubility and the advent of a different phase. This is the formation of the so-called "electron compounds." It was observed first by HUME-ROTHERY that these

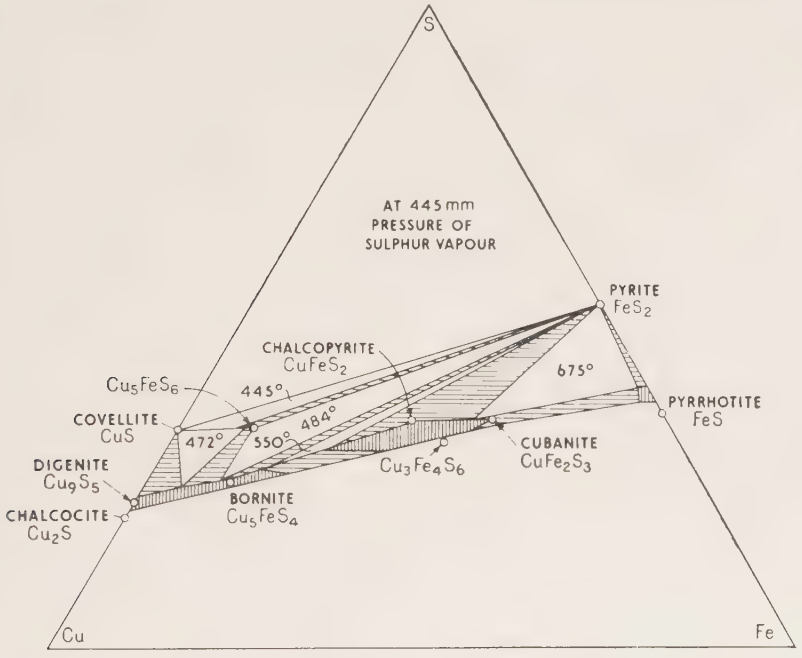

Fig. 1. The Ternary System Cu-Fe-S at 455 mm sulphur vapour pressure (after MERWIN and LOMBARD, 1937).

compounds corresponded to definite ratios of free electrons to atoms. The copper-zinc system is the classical example of the formation of this type of compound. Considerable zinc will go into the face-centred cubic copper or α-brass structure, but when enough zinc is added to bring the free electron to atom ratio up to 3 : 2 (zinc contributes two free electrons while copper can contribute but one) then the body-centred β-brass phase is formed. An explanation for the existence of these compounds consistent with the modern electron theory of metals was advanced by H. JONES (1937). This may be briefly summarized as follows.

The first Brillouin zone for the face-centred cubic copper or α-brass structure, as well as for the body-centred β-brass structure, can contain two electrons per atom. However, this first zone, whose surface represents discontinuities in the energy states that can be occupied by the free electrons in the periodic field of the crystal, in the face-centred cubic case is made up of the octahedron {111} truncated by the cube {200}, while in the body-centred cubic crystal it is formed

by the dodecahedron {110}. The surface of the Fermi body of pure copper with its one free electron per atom will be well within the first Brillouin zone (Fig. 2a). The Fermi surface represents the highest energy level in momentum or wave number (k) space that is attained by the free electrons in the metal. When more

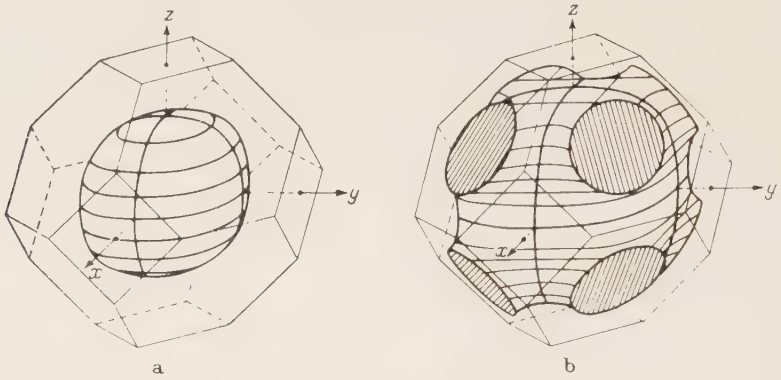

Fig. 2. The first Brillouin zone of the face-centred cubic structure with (a) The Fermi surface of occupied states well within the zone, (b) With the Fermi surface touching the zone boundary (after Hume-Rothery, 1946).

electrons are added to the metal by substituting zinc atoms, with two electrons to donate, for copper atoms, the additional electrons must occupy higher states (Pauli exclusion principle) and the Fermi body becomes larger in all directions until it touches the Brillouin zone (Fig. 2b). This contact occurs at an electron-to-atom ratio of 1·36. As the number of free electrons is increased there become

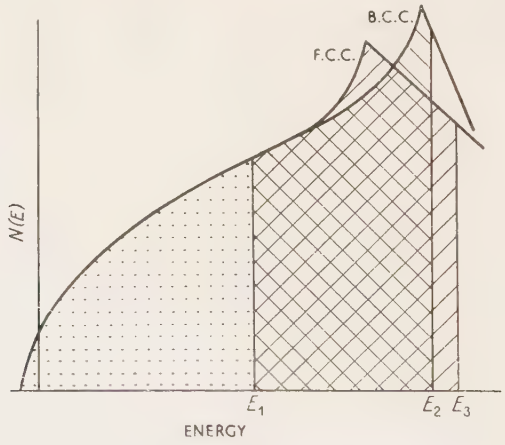

Fig. 3. Number of energy states per unit energy range as a function of energy for the face-centred and body-centred cubic structure (adapted from Jones, 1937).

available fewer low-energy states because the Brillouin zone now presents a barrier for certain directions and successive electrons more rapidly fill the remaining volume of the zone at higher and higher energy levels. It is at this point that the switch to the body-centred structure of β-brass becomes advantageous, because the Brillouin zone surface of this latter structure is not reached until we

have an electron-to-atom ratio of 1·48, which means there are more states of lower energy level available for the free electrons in the body-centred structure than there are in the face-centred structure. Perhaps this can be more easily seen from the $N(E)$ vs. E curves for the two structures (Fig. 3). $N(E)$ is the number of electrons per unit volume of metal for a very small energy range of $E + dE$ and it is plotted against the energy of the electron E. For pure copper the electrons will occupy the stippled area up to E_1. If enough zinc were added to make the electron-to-atom ratio 3 : 2, then, in addition to the stippled area, that portion shaded by slanting lines of positive slope which reaches a level of E_3 would give the states occupied if the f.c.c. structure were maintained, while that portion shaded by slanting lines of negative slope which reaches a level of E_2 would give the states occupied if the b.c.c. structure were formed. Therefore, as metals tend to crystallize in structures that allow all the electrons to be at the lowest possible energy level, the b.c.c. structure is to be preferred.

Application to Sulphides

Before applying the above ideas in an attempt to explain the stability of certain sulphide phases, it would be well to note wherein these sulphide systems differ from metallic systems. Perhaps the most significant difference lies in the variations of electrical conductivity with temperature and composition. Most metals are classed as true conductors, and copper, α-brass and β-brass mentioned in the preceding sections are not exceptions. Consequently, at low temperatures they are good conductors and their conductivity varies inversely with the temperature. In zone theory this means that their Fermi body can undergo a displacement in momentum space in response to an applied field. Resistivity is caused by the collision of electrons with phonons (thermal vibration of the lattice) which of course increases with temperature. On the other hand the sulphides in the copper-rich side of the Cu-Fe-S diagram (Fig. 1) can be considered as intrinsic semi-conductors (Frueh, 1950; Eisenmann, 1952), which means that the conductivity is very low at low temperatures and increases with increasing temperature. Intrinsic semi-conductors are represented in zone theory as having a Brillouin zone which is just filled and an energy gap of forbidden states between the filled zone and the next zone. Conductivity takes place because electrons receive a boost across the forbidden band by thermal energy (collision with a phonon) and become conducting electrons in a higher zone, while the hole they vacated facilitates a change in the momentum states of the electrons in the lower zone.

Less tolerance for substitution solid solution between atoms having a different number of free electrons to donate can be expected in a compound whose Brillouin zones are filled. This will be especially true for the substitution of an atom donating a large number of free electrons in place of one donating few, as any additional electrons must seek a much higher energy level. Such a substitution could occur and not require the elevation of an electron to a higher energy level if it were accompanied by the omission of one of the constituent atoms from the structure. It should be noted, however, that this vacancy would cause an increase in the total energy of the compound. The number of substitutions that could take place per vacancy would depend upon the free electron contribution of the atom omitted

and the difference in free electron contribution between the original and substituting atoms. In a compound occurring in ternary or higher systems, substitution could occur between two species of atoms, and vacancies could occur in the positions normally occupied by a third species.

The principal Brillouin zones of the minerals of the copper-rich side of the Cu-Fe-S system and the electron-to-atom ratios necessary to fill these zones are listed in Table 1. The details involved in the computation of these zones are contained in the appendix at the end of this paper.

Table 1

Mineral	*Indices of forms determining principal zones*	*Electron to atom ratio of filled zone*
Chalcopyrite ($CuFeS_2$)	{112} {200} {004}	1
	{204} {220}	4
Bornite* (Cu_5FeS_4)	{311} {222}	0·5
	{400}	1·6
	{440}	3·2
Digenite (Cu_9S_5)	{200}	1·4
	{220}	2·9
Chalcocite* (Cu_2S)	{102} {110}	1·7
	{103} {110}	3·3
Covellite (CuS)	{102} {103}	0·5
	{110} {006}	1·5

* The higher temperature forms of these minerals were used because the intense diffraction lines that determined the principal zones were common to both high and low forms.

If we assume that all the outer shell electrons of the elements of this ternary system could contribute to the free electrons composing the Fermi body, then copper would yield one free electron, iron would yield three and sulphur six. Iron, being a transition metal, is seldom credited with contributing as many as three electrons when combined with other metals in intermetallic phases. It should be noted that in intermetallic compounds the iron invariably has co-ordination higher than tetrahedral. With the foregoing assumption, chalcopyrite would have 4 electrons per atom; bornite would have 3·2; digenite, 2·8; chalcocite, 2·7; and covellite, 3·5.

The electrons of the first three minerals nicely fill one of the important Brillouin zones; digenite somewhat less perfectly than the others. At elevated temperatures the disordered form of each of these minerals (no ordered form of digenite has ever been described) belongs to a single solid solution series (Schlegel and Schuller, 1952). The ordered phases that exist at lower temperatures have a common basic structure that can be looked upon as composed of cubic close-packed sulphur atoms with the interstitial tetrahedral holes being in part occupied by

the metal atoms. It should be noted that in each instance the Brillouin zone just filled is that constructed from the same basic reflections. As iron with its three electrons is substituted for copper with its one, it is necessary to substitute holes to prevent raising electrons to higher energy levels. This is done by eliminating some of the metal atoms, which changes the sulphur-to-metal ratio. This in turn increases the atomic volume which increases the electron-to-atom ratio permissible. Consequently, a line can be drawn in the ternary diagram from digenite through bornite to chalcopyrite along which all compositions will exactly fill their Brillouin zones. Deviations away from this line will require either raising the electrons to higher energy levels, leaving the zone unfilled, or substituting holes for sulphur atoms. It is to the latter two possibilities that the width of the field can be attributed.

Extension of the field away from sulphur will be more limited than the extension along the digenite-chalcopyrite line because the increase in energy caused by the occurrence of vacancies in the face-centred sulphide positions is likely to be larger than the increase caused by vacancies in the interstitial metal positions.

Chalcocite with 2·7 e/a and covellite with its 3·5 e/a do not appear to fit nicely in any zone. However, two structural types of copper and sulphur atoms are present in covellite. One type of sulphur is tied up in S_2 groups and it has been suggested that the formula be written $Cu_3S\,S_2$ rather than CuS (Bragg, 1937). If the sulphur atoms involved in the S_2 group do not contribute any electrons to the Fermi gas, then the electron-to-atom ratio will fall to 1·5 which will exactly fill one of the zones. The structure of chalcocite has not as yet been determined, but if a similar condition with the inclusion of S_2 groups exists and the formula can be written $Cu_8S_2S_2$, then the electron-to-atom ratio would be 1·7 which would exactly fill one of its zones.

Substitution of iron for copper in the structure of chalcocite and covellite may be more difficult to achieve because the energy accompanying a vacancy that will be created to avoid accommodating electrons at higher energy states may be greater in these more complex structures than in the simpler digenite-chalcopyrite type.

Summary

The stability of any mineral assemblage is dependent upon the total energy of that assemblage compared with any other assemblage of the same total composition. In sulphide minerals where the cohesive forces appear to be metallic in nature, an important part of the energy is due to the energy states of the free electrons. The periodic structure of the mineral determines bands or zones of energy levels that can be occupied by the electrons. A structural type is maintained despite changes in composition when the electron-to-atom ratio necessary to fill one of its Brillouin zones is maintained. To accomplish this, vacancies are created in certain positions. These vacancies increase the energy of the crystal in varying degrees depending upon the importance of the original position in maintaining the structure. The copper-rich portion of the Cu-Fe-S system is illustrative of these effects. Because of the questionable contribution of free electrons by transition metals, precise magnetic and electrical measurements are needed to analyze successfully the iron-rich portion of the system on the same basis.

Calculations of the energy states of free electrons and energies connected with vacancies have been made for close-packed metals and structurally simple compounds. However, the computation of these energies for more complex compounds such as those we are dealing with above would be almost prohibitive. Simplifying assumptions would have to be made that would introduce much inaccuracy. It therefore seems justifiable to present this qualitative and perhaps somewhat intuitive picture.

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Appendix

Determination of Brillouin zones

The surface or boundaries of the Brillouin zones represent locations of discontinuities in the continuum of energy states permissible to the free electrons in the periodic field of a crystal structure. They have dimensions related to the energy or momentum of the electron. The most convenient unit is that of wave number k defined as equal to $\frac{2\pi}{\lambda}$ where λ is wavelength. The wavelength is indirectly proportional to the momentum of the electron, the constant of proportionality being Planck's constant.

In the periodic structure of a crystal, electrons are diffracted in the same manner as x-rays; i.e., in accordance with Bragg's law ($n\lambda = 2d \sin\theta$). The effect of this diffraction is to change the directions and momentum of the electron. For every direction in the crystal there are specific values of λ or $\frac{2\pi}{\lambda}$ for which this change takes place. Because of the aforementioned relation between wavelength and energy or momentum, this value also represents a point of discontinuity in a continuum of energy states and constitutes a point on the surface of the Brillouin zone. It follows that the Brillouin zone of any crystal can be computed from a knowledge of the diffraction record of the crystals. An exact and detailed treatment of these calculations can be found in texts on modern solid state theory.

The more useful unit in applying zone theory is the electron-to-atom ratio necessary to fill a zone. Each zone possesses a definite volume which is a measure of 1/2 the number of electron states comprising the zone. (The Pauli exclusion principle permits two electrons of opposite spin to occupy each energy state.) Therefore, twice the volume of the zone multiplied by the atomic volume (i.e., the volume of the unit cell divided by the total number of atoms per cell) will equal the electron-to-atom ratio necessary to fill the zone.

Except where so indicated, all the diffraction data reported were taken with a Guinier type focusing camera using monochromatic cobalt $K\alpha$ radiation. Only the forms yielding intense reflections were considered.

Chalcopyrite $CuFeS_2$

Tetragonal: $142d$: $a = 5{\cdot}24$ Å, $c = 10{\cdot}30$ Å, $a : c = 1 : 1{\cdot}966$ (Palache, Berman and Frondel, 1944). Atomic volume $\frac{a^2c}{16}$ Å^3 per atom

hkl	*I*	*d*	*hkl*	*I*	*d*
101	very weak	4·67	004	medium	2·57
112	very strong	3·01	211	very weak	2·28
103	very weak	2·87	220	strong	1·853
200	medium	2·62	204	strong	1·836

The first important zone is made up from the {112} {220} and {004} reflections. Its volume is:*

$$V = 4\int_0^{2/c} \left(\frac{\sqrt{Q}}{c} - \frac{2a}{c}\,y\right)^2 dy - 4\int_{1/a}^{\sqrt{Q}/c} \left(\frac{Q}{ac} - \frac{2\sqrt{Q}}{a}\,x + \frac{c}{a}\,x^2\right) dx$$

where $Q = 4 + \frac{4a^2}{c^2} + \frac{c^2}{a^2}$

Although the axial ratio $a : c$ possibly varies with composition it is very close to 1 : 2. For the present work this value shall be assumed, as it greatly simplifies the above expression, and the volume becomes $\frac{4}{a^3}$. With the same assumption as to axial ratio, the atomic volume becomes $\frac{a^3}{8}$. This zone can therefore contain 1 free electron per atom.

The second important zone is made up from the {220} and {204} reflections. Its volume is:

$$V = 8\int_0^{\sqrt{R}/a} \left(\frac{2\sqrt{R}}{c} - \frac{2a}{c}\,y\right)^2 dy - 8\int_{\frac{\sqrt{2}R}{c}}^{\frac{2\sqrt{2}R}{c}} \left(\frac{2\sqrt{2}}{a} - x\right)\left(\frac{\sqrt{R}}{a} - \frac{cx}{2a\sqrt{2}}\right) dx$$

where $R = 2 + \frac{c^2}{4a^2} + \frac{4a^2}{c^2}$

* The expression for the volume in this instance is more compact before integrating, and as it may prove interesting to investigate changes in axial ratio with composition, it is being included.

If the axial ratio is assumed to be 1 : 2 the volume becomes $\frac{16}{a^3}$ which permits this zone to contain 4 free electrons per atom.

Bornite Cu_5FeS_4

The faint superstructure lines that exist in various ordered forms (TUNELL and ADAMS, 1949; FRUEH, 1950) of this mineral of perhaps questionable composition, have been ignored.

Cubic $Fd3m$; $a = 10{\cdot}93$ Å. Atomic volume $\frac{a^3}{8}$ Å^3.

hkl	*I*	*d*	*hkl*	*I*	*d*
311	strong	3·30	331	medium	2·50
222	strong	3·15	333	weak	2·10
400	strong	2·72	440	very strong	1·92

The first zone is made up from the {311} and {222} reflections. It volume is $\frac{21{\cdot}6}{a^3}$ and can contain 0·5 electrons per atom. The next important zone would be determined by the {400} reflections and have a volume of $\frac{64}{a^3}$ and could contain 1·6 electrons per atom. The {440} will determine the next zone with a volume of $\frac{128}{a^3}$ that can accommodate 3·2 electrons per atom.

Digenite Cu_9S_5

The cell and composition of this mineral were established by N. BUERGER (1942) but the symmetry assumed to be isometric has not been determined in detail. The following powder data are compiled from spacings listed by BUERGER, while the intensities come from BARTH (1926).

Cubic (?) $a = 5{\cdot}56$ Å (PALACHE, BERMAN and FRONDEL, 1944). Atomic volume $\frac{a^3}{11{\cdot}2}$ Å^3.

hkl	*I*	*k*	*hkl*	*I*	*d*
111	weak	3·25	220	very strong	1·95
200	medium	2·78	311	medium	1·6

The zone compiled from the {200} reflections has a volume of $\frac{8}{a^3}$ and can contain 1·4 electrons per atom. The zone constructed from the {220} reflections possesses a volume of $\frac{16}{a^3}$ and can contain 2·8 electrons per atom. Another possible zone is that determined by the {311} reflections with a volume of $\frac{40}{a^3}$ and a capacity of 7·1 electrons per atom.

Chalcocite Cu_2S

Although this mineral exists in several modifications, the most intense x-ray reflections are common to both. For ease of computation, the symmetry and indexing of the high form has been used.

Hexagonal: H6/ mcm; $a = 3{\cdot}89$ Å, $c = 6{\cdot}68$ Å, $a : c = 1{\cdot}717$ (Buerger and Buerger, 1944). Atomic volume $\frac{a^3}{4{\cdot}03}$ Å^3.

hkl	*I*	*d*	*hkl*	*I*	*d*
101	medium	3·01	110	strong	1·94
102	strong	2·37	103	strong	1·86

The first Brillouin zone determined by the {102} and the {110} has a volume of $\frac{3{\cdot}4}{a^3}$ and a capacity of 1·7 electrons per atom. If the zone were constructed from the {102} reflections alone, then it would have a volume of $\frac{3{\cdot}6}{a^3}$ and could contain 1·8 electrons per atom. The next important zone is made up from the {103} and {110} reflections. It has a volume of $\frac{6{\cdot}65}{a^3}$ and can contain 3·3 electrons per atom.

Covellite CuS

Hexagonal: C6/mmc; $a = 3{\cdot}802$ Å, $c = 16{\cdot}43$ Å, $a : c = 1 : 4{\cdot}32$ (Palache, Berman, and Frondel, 1944). Atomic volume $\frac{a^3}{3{\cdot}21}$ Å^3.

hkl	*I*	*d*	*hkl*	*I*	*d*
100	very weak	3·26	103	very strong	2·79
101	weak	3·20	006	strong	2·71
102	strong	3·02	110	strong	1·88

The first important zone is determined by the {102} and {103} reflections. It has a volume of $\frac{0{\cdot}746}{a^3}$ and a capacity of 0·47 electrons per atom. If this zone is further truncated by the {006} reflections, its volume will reduce to $\frac{0{\cdot}671}{a^3}$ and its capacity to 0·418 electrons per atom.

The {110} and {006} reflections determine the next important zone which has a volume of $\frac{2{\cdot}40}{a^3}$ and can contain 1·5 electrons per atom.

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Trace element variation during fractional crystallization as calculated from the distribution law

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ABSTRACT

Assuming that the distribution law is valid under the P-T-X conditions concerned, a general outline is given of the distribution of trace elements between several phases formed in a crystallizing magma.

The variation in the distribution coefficients with temperature and chemical composition is discussed.

It is shown that extreme care must be taken when distribution coefficients are determined by a study of naturally occurring rocks, and that a determination may, in many cases, be impossible.

The distribution of trace elements between rocks formed by crystallization of magmas is governed by (1) the laws of crystallization of minerals from magmas, and (2) the laws of distribution of trace elements between the minerals formed.

Although petrogenetical problems are still abundant, the laws of crystallization of minerals from magmas are fairly well known after a century's intensive petrological research and half a century's study of crystallization of artificial melts mainly conducted in the Geophysical Laboratory in Washington.

The distribution of a trace element between rock forming minerals depends entirely on its diadochical properties. In this connection it is of interest to note that six of the nine papers by V. M. Goldschmidt on Geochemische Verteilungsgesätze der Elemente dealt with crystal chemistry, and in these he was able to demonstrate that the conditions for isomorphism and solid solubility are mainly dependent on ionic radii and also on type of chemical bonding. In 1937 he formulated the so-called Goldschmidt's rules of camouflage, capture, and admission, which have since been widely used as a basis for discussion of the distribution of trace elements. It has been generally felt by geochemists that these rules were an over-simplification, but only recently has it been considered in detail in an important paper by D. M. Shaw (1953).

In the present paper an attempt is made to give a general theoretical discussion of the distribution of trace elements between minerals crystallizing from a magma, based on the distribution law.

The distribution law states that there is a constant ratio between the concentrations (strictly speaking, activities) of any given component in any two phases of a system in equilibrium at constant temperature and pressure. If the general law be applied to the present problem, it states that if a number of minerals crystallize from a magma at a certain temperature and pressure, a trace element present in the magma will distribute itself between the magma and the several minerals in such a way that $\frac{\text{conc. in mineral } a}{\text{conc. in mineral } b} = K_{ab}$, $\frac{\text{conc. in mineral } a}{\text{conc. in magma}} = K_a$, and $\frac{\text{conc. in mineral } b}{\text{conc. in magma}} = K_b$, where K_{ab}, K_a, and K_b are mathematical constants

independent of the concentration of the trace element. The following simple equation exists between these coefficients[1] $K_{ab} = \frac{K_a}{K_b}$.

The distribution law as stated above is only approximate. K_{ab}, K_a, K_b, etc., are not mathematical constants as will be seen by studying a bicomponent system, e.g., the olivine system Mg_2SiO_4–Fe_2SiO_4. If in this case Fe be regarded as distributing itself between forsterite and melt, the distribution law states that $K = \frac{\text{concentration of Fe in forsterite}}{\text{concentration of Fe in melt}} = \frac{x}{y}$ in Fig. 1, and it will be seen that K varies from 0·2 on the left-hand side to 1·0 on the right-hand side of the diagram. By regarding K as a mathematical constant, we are expressing the distribution in

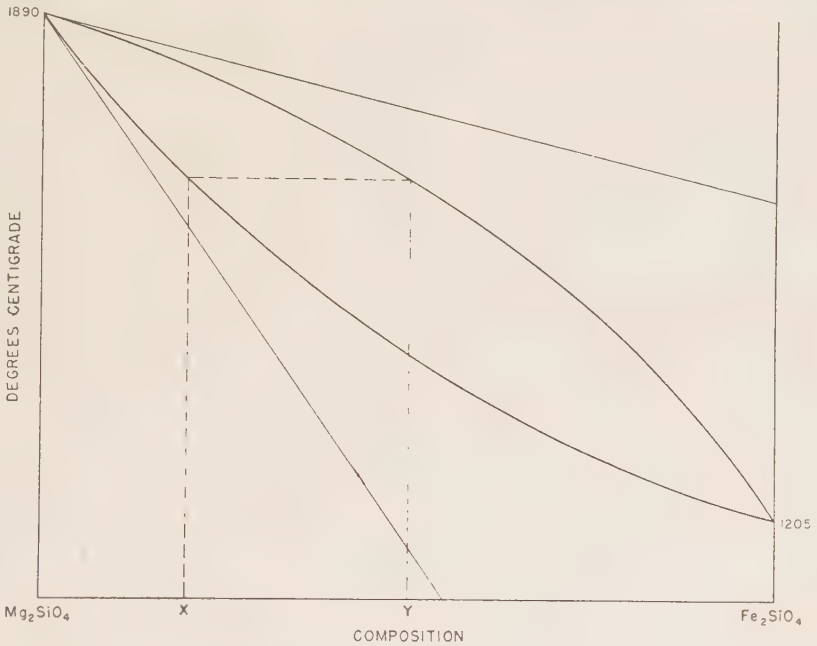

Fig. 1. The system forsterite-fayalite with tangents drawn to the solidus and liquidus curves.

terms of the tangents to the solidus and liquidus curves at the zero point (see Fig. 1) instead of in terms of the curves themselves. The use of the distribution law as a basis for the present discussion instead of the more complicated mathematical expressions for the solidus and liquidus curves introduces an error which is, however, negligible as long as the concentration of the trace element is low, say less than one per cent.

The distribution coefficients (K_a, K_b, and K_{ab} above) may also be expressed as functions of the partial vapour pressures of the trace element in the phases concerned. The partial vapour pressures vary with temperature and also with

[1] In this paper distribution coefficient will be used as a general term, while the special term distribution factor will be used to designate distribution coefficients describing the distribution of a trace element between a mineral and a magma.

composition in non-ideal solutions. It follows that the distribution coefficients will vary with the changing temperature and composition of the solidifying magma. This variation in the coefficients will be discussed later, but before doing so, it may be of interest to outline what happens to trace elements in crystallizing melts if we assume that the distribution coefficients do not vary with temperature and composition, an assumption which may not represent, in some cases, a satisfactory approximation of true conditions.

In order to study the concentration of a trace element in the solid phases of a crystallizing melt, it is convenient first to consider the variations of the concentration of the trace element in the melt itself. The concentration of the trace element in any solid phase is then obtained by the simple application of the distribution factor K at any point in the system in question.

The following differential equation for a single component system can be written according to the definition of the distribution factor K:

$$\frac{dm}{ds} = K\left(\frac{M - m}{Q - s}\right) \tag{1}$$

where Q = original quantity of melt
M = original quantity of trace element in the melt
s = quantity of solid phase
m = quantity of trace element in the solid phase
K = distribution factor

The solution of this equation (1) can be written as follows:

$$m = M\left(1 - \left(1 - \frac{s}{Q}\right)^K\right) \tag{2}$$

The concentration of the trace element in the solid phase and in the melt at any point in the crystallization can be obtained in terms of the variable s by differentiation of equation (2)

Thus

$$c_s = \frac{dm}{ds} = K\frac{M}{Q}\left(1 - \frac{s}{Q}\right)^{K-1} \tag{3}$$

and

$$c_q = \frac{c_s}{K} = \frac{M}{Q}\left(1 - \frac{s}{Q}\right)^{K-1} \tag{4}$$

where c_s = concentration of trace element in solid phase
c_q = concentration of trace element in melt

Similar expressions were developed independently by McFEE (1947) in a study of the capture of "impurities" by artificially grown NaCl crystals, by NEUMANN (1948) in a theoretical study of hydrothermal differentiation, and by HOLLAND and KULP (1949) in a theoretical study of the distribution of accessory elements in pegmatites.

Equation (4) can be applied to systems involving two or more solid components if the combined behaviour of the solid phases can be described by a constant combined distribution factor. Such a combined distribution factor can be applied to a system under the following conditions:

(a) The distribution factors for each separate solid phase must be constant.

(b) The proportion of each solid phase in the total solid phase must be constant.

It is quite evident that most systems are too complex to satisfy these conditions throughout the entire process of crystallization; however, most systems can be divided into a series of separate stages in which these conditions are moderately well satisfied. (Equation (4) cannot be applied if the melt reacts with a solid phase formed in a previous stage.)

Assuming the conditions noted above, the value of the combined distribution factor (K') can be expressed as follows: (HOLLAND and KULP, 1949)

$$K' = r_1K_1 + r_2K_2 + \ldots r_nK_n \tag{5}$$

where K_1, K_2, etc. = Distribution factors for solid phases 1, 2, etc.

$$r_1, r_2, r_n = \frac{\text{Quantity of solid phase 1, 2, or } n}{\text{Total quantity of solid phase formed during stage}}$$

Equation (4) thus can be applied to a given stage of a multi-component system by the substitution of K' for K. The values of Q and M then refer to the values at the beginning of the particular stage and s refers to the solid phase crystallized during that stage.

In many systems resorption of one or more of the solid phases during crystallization must be considered. Let us assume that during a particular stage in the crystallization of a melt one solid component is resorbed at a constant rate. Equation (1) can then be rewritten as follows:

$$\frac{dm}{ds} = K\left(\frac{M - m + c_r P s}{Q - (1 - P)s}\right) \tag{6}$$

where c_r = Average concentration of trace element in the resorbed solid phase

$$P = \frac{\text{Quantity of solid phase resorbed during stage}}{\text{Quantity of solid phase formed during stage}}$$

Q = Quantity of melt at beginning of stage

s = Quantity of solid phase formed

Conventional solution of this linear, first order equation yields the following:

$$m = M + \frac{c_r PQ}{1 - P} + \frac{Kc_r P(Q - (1 - P)s)}{(1 - P)(1 - P - K)} - M\left(1 - \frac{(1 - P)s}{Q}\right)^{\frac{K}{1-P}} - \frac{c_r PQ}{1 - P - K}\left(1 - \frac{(1 - P)s}{Q}\right)^{\frac{K}{1-P}} \tag{7}$$

Expressions for c_s and c_q are obtained by differentiation as before.

$$c_s = \frac{dm}{ds} = \frac{Kc_r P}{1 - P - K}\left(\left(1 - \frac{(1 - P)s}{Q}\right)^{\frac{K}{1-P}-1} - 1\right) + \frac{KM}{Q}\left(1 - \frac{(1-P)s}{Q}\right)^{\frac{K}{1-P}-1} \tag{8}$$

$$c_q = \frac{c_s}{K} = \frac{c_r P}{1 - P - K}\left(\left(1 - \frac{(1 - P)s}{Q}\right)^{\frac{K}{1-P}-1} - 1\right) + \frac{M}{Q}\left(1 - \frac{(1 - P)s}{Q}\right)^{\frac{K}{1-P}-1} \tag{9}$$

The special case for $K = 1 - P$ must be handled separately as equations (7), (8), and (9) involve an indeterminate. Evaluation of this indeterminate by conventional methods reduces equation (9), for example, to the following:

$$c_q = \frac{c_r P}{1 - P}\ln\left(1 - \frac{(1 - P)s}{Q}\right) + \frac{M}{Q} \tag{10}$$

For systems involving several solid phases as well as resorption, the above equations may be used with values of the combined distribution factor K' for any particular stage.

Application of equation (4) to a single component system yields the family of curves shown in Fig. 2. Here the concentration of the trace element in the melt (c_q) is plotted as a function of the degree of solidification. The concentration of the trace element in the solid phase is, by definition, K concentration in melt (see Fig. 3).

A stage in a multi-component system is described by this same family of curves, if one substitutes the combined distribution factor K' for K. It should be noted that in all but the last stage of a multicomponent system, the curve will end at some value of s/Q less than 1. The trace element concentration in each solid phase is again obtained by multiplying the c_q curve by the value of K for each phase.

It is desirable to combine the curves for the individual stages of a system into a single set of curves that describe the entire system. This can be done by adjusting the value of c_q at the beginning of each stage to the value of this quantity at the end of the preceding stage, and by transforming the values of s/Q for each stage to conform with the values for the entire system.

The results for a stage in which resorption must be considered can be plotted in much the same manner. Equation (9) is applied in this case using the proper values for c_r, P, and K or K' according to the system in question. The combining of the curves for a series of such stages into a single plot of the entire system is slightly more complicated. One must remember that the quantity s for a single stage (equation 9) refers only to the solid phase formed in that stage. Thus, in the extreme, a change in s for a single stage might be equivalent to little or no change in the total quantity of solid phase in the system.

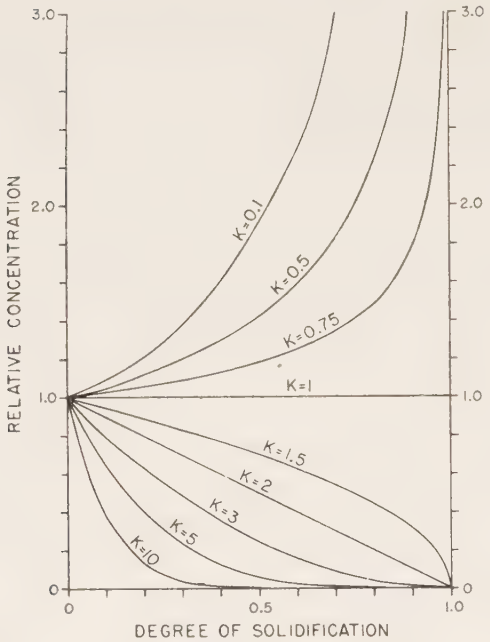

Fig. 2. Variation in the concentration of a trace element in a melt with degree of solidification for different values of the distribution factor, K.

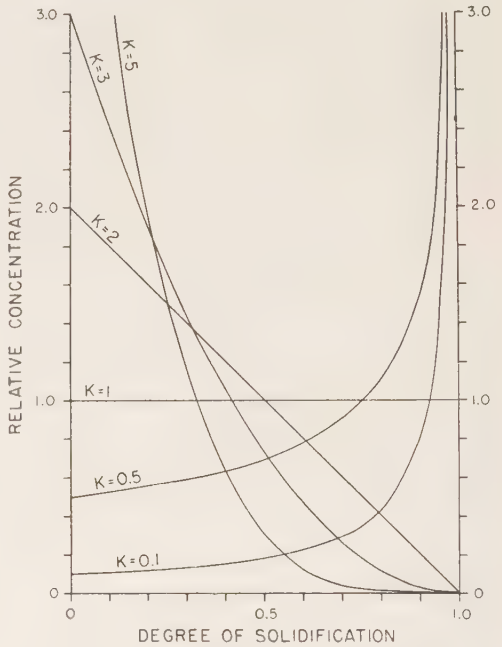

Fig. 3. Variation in the concentration of a trace element in a solid with degree of solidification of the melt for different values of the distribution factor, K.

The general trends in the distribution of trace elements as governed by the above equations can be best illustrated by examples from artificial melts.

The enrichment or impoverishment of a trace element in early crystals as compared to late crystals in a one-component system for varying values of the distribution factor K is illustrated by Fig. 3.

Fig. 4 shows the distribution of a trace element between the phases of a two-component system with a eutectic, in this case the system anorthite-leucite (Schairer and Bowen, 1947). Let us consider a melt of composition 90% anorthite and 10% leucite. It is assumed that the trace element concerned has a distribution factor for anorthite, $K_{An} = 2$, and a distribution factor for leucite, $K_{Leuc} = 4$. As the crystallization of anorthite proceeds, the concentration of the trace element in melt and mineral alike will decrease, and by the time the eutectic is reached and leucite also begins to crystallize, the melt is sufficiently impoverished to give a comparatively low concentration of the trace element in leucite in spite of its high distribution factor. With the distribution factors chosen the trace

element is more easily admitted to the leucite lattice than to the anorthite lattice as illustrated by the distribution coefficient $K_{\text{Leuc, An}} = K_{\text{Leuc}}/K_{\text{An}} = 2$. However, if we analyzed these minerals for their trace element content, the opposite relationship would be apparent. The concentration in anorthite would be found to be 0·99, and in leucite 0·26 (the original concentration in the melt being chosen as unity), giving an apparent distribution coefficient of 0·26 as different from the correct value of 2·0. This example illustrates very clearly that when crystals in

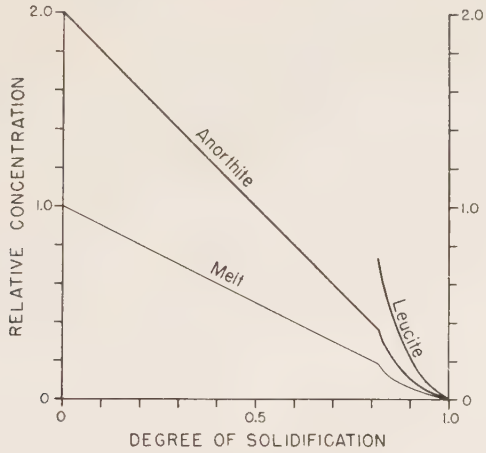

Fig. 4. Distribution of a trace element between anorthite and leucite crystallizing from a melt of composition An 90, Leuc 10. The assumed distribution factors for the trace element are $K_{\text{An}} = 2$, and $K_{\text{Leuc}} = 4$.

a natural rock are selected for determination of distribution coefficients, they must not merely have formed under equilibrium conditions but they must also have formed at the same time if serious errors are to be avoided. Because of the difficulty of finding decisive criteria of contemporaneity, a determination of distribution coefficients of rock forming minerals may in very many cases be rendered impossible.

The system anorthite–forsterite–silica (Andersen, 1915) has been chosen to illustrate the conditions in a multi-component system. For a melt of composition An 25, Fo 60, SiO_2 15, let us choose arbitrarily two sets of distribution factors for forsterite, enstatite, anorthite, and silica: $K_{\text{Fo}} = 3$, $K_{\text{En}} = 1{\cdot}5$, $K_{\text{An}} = 0{\cdot}1$, $K_{SiO_2} = 3$; and $K_{\text{Fo}} = 1{\cdot}5$, $K_{\text{En}} = 3{\cdot}0$, $K_{\text{An}} = 1{\cdot}5$, $K_{SiO_2} = 0{\cdot}5$. For each example two different cases must be considered.

(a) The melt remains in equilibrium with the crystalline phases during its solidification, in which case a resorption of olivine will take place from the time enstatite begins to form after 37 per cent of the magma has crystallized.

(b) The crystals are removed from the melt as soon as they are formed, in which case no resorption can take place, and silica will crystallize from the melt in the last stage of solidification.

The actual course in natural magmas would probably most often lie between these two extremes.

The distribution of a trace element in the system anorthite–forsterite–silica

has been calculated on the above assumptions and the results are given in Figs. 5 and 6. The diagrams are self-explanatory, but a few important features may be pointed out.

As was also apparent from Fig. 2, the restmagma has unique properties, since any trace element will either be strongly enriched in, or will be virtually removed from the magma towards the end of crystallization.

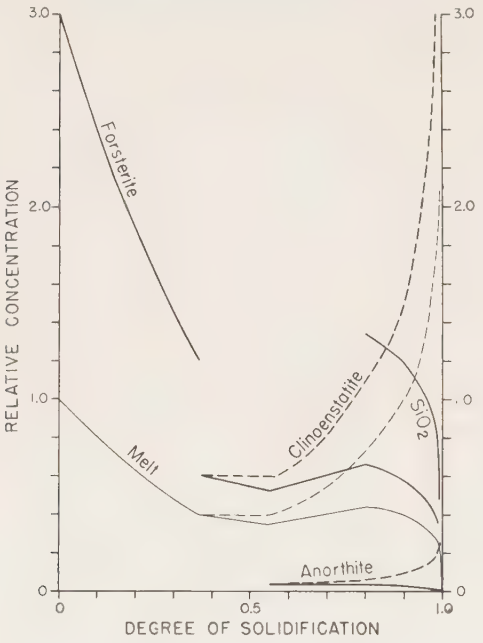

Fig. 5. Distribution of a trace element between minerals formed from a melt of original composition Fo 60, An 25, SiO_2 15. The assumed distribution factors are $K_{Fo} = 3$, $K_{En} = 1{\cdot}5$, $K_{An} = 0{\cdot}1$, $K_{SiO_2} = 3$. Dashed lines illustrate distribution when early formed olivine is resorbed, and solid lines when no resorption takes place.

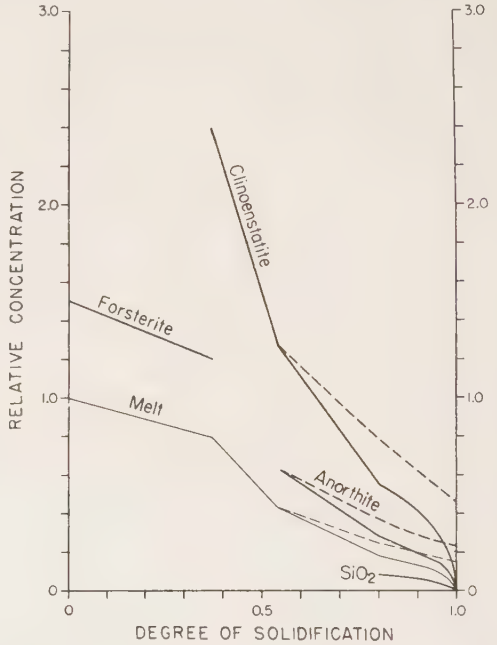

Fig. 6. Distribution of a trace element between minerals formed from a melt of original composition Fo 60, An 25, SiO_2 15. The distribution factors chosen as $K_{Fo} = 1{\cdot}5$, $K_{En} = 3{\cdot}0$, $K_{An} = 1{\cdot}5$ $K_{SiO_2} = 0{\cdot}5$. Dashed lines illustrate distribution when early formed olivine is resorbed, and solid lines when no resorption takes place. (In the early stage of crystallization of clinoenstatite the effect of resorption is too small to be shown.)

The conditions under which a magma crystallizes may be of decisive importance to the fate of a trace element as illustrated by Fig. 5. This shows an enrichment in the restmagma if resorption is allowed to take place, or an impoverishment if resorption does not take place (e.g. because of crystal settling or squeezing out of magma during solidification).

As was indicated in the discussion of Fig. 4, the age relationships are equally as important as the distribution factors in considering the distribution of trace elements between minerals.

The above discussion is based on the assumption that the distribution coefficients are mathematical constants. As already mentioned, this does not hold true. They vary with temperature, pressure, and chemical composition of the solidifying magma.

The variation with change in temperature will be dealt with in a qualitative way. Let us consider a system of two minerals, a magma, and a trace element distributed between these three phases. For this system to be in equilibrium, the partial vapour pressures of the trace element in each of the three phases must be the same. If now the temperature is changed from T_1 to T_2 the partial vapour pressures of the trace element in the three phases will also change, as also will the ratios between them. To restore equilibrium, it is obviously necessary to adjust

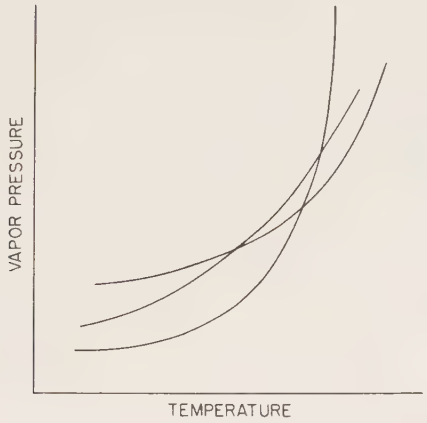

Fig. 7. Vapour pressure curves.

the concentrations of the trace element in the three phases in such a way that the partial vapour pressures will again be equal. For this qualitative treatment RAOULT'S law can be regarded as valid, and hence the partial vapour pressure of the trace element in any phase assumed proportional to its concentration in that phase. Let n be the factor by which the ratio of the vapour pressures in any two phases a and b has changed due to the change in temperature from T_1 to T_2. If now the concentrations of the trace element are readjusted in such a way that the ratio between the concentration in a and that in b is changed by a factor of $1/n$, the ratio of the partial vapour pressures will be changed by the same factor, and the system is again in equilibrium. By definition the distribution coefficient $K_{ab} = \frac{\text{concentration of trace element in } a}{\text{concentration of trace element in } b}$; by the change in temperature from T_1 to T_2 the distribution constant, therefore, has been changed by a factor of $1/n$. With variation in temperature the distribution coefficients vary reciprocally with the ratios between the partial vapour pressures of the trace element in the phases concerned.

The general trend of vapour pressure curves is shown in Fig. 7. If we regard the three curves drawn as representing the partial vapour pressures of a certain trace element in two minerals and a magma, it is easily seen that any one of the three distribution coefficients implied may be approximately constant within a certain range of temperature while it may show a high degree of variation within another temperature range. It is also worthy of notice that a distribution coefficient may at a certain temperature change from > 1 to < 1 or *vice versa*, which

means that a mineral crystallizing from a magma may remove a trace element from that magma at a high temperature, while at a lower temperature, the magma may be enriched in the same trace element by crystallization of the same mineral.

In ideal solutions the vapour pressure is independent of the composition of the solvent. The naturally occurring silicate magmas are, however, far from being ideal solutions. Within the range of temperature of their solidification at least, they are in a pseudocrystalline state related to that of crystalline silicates. The silicon-oxygen tetrahedra of the magma are linked together in one-, two-, or three-dimensional networks while the bulk of the cations occupy no fixed positions. In very basic magmas most of the silica is present as individual silicon-oxygen tetrahedra while the tendency to formation of networks increases with increasing silica content. The bonding properties of unlinked silicon-oxygen tetrahedra and the several types of silicon-oxygen networks are different in crystalline silicates (Ramberg, 1952), and we will therefore expect them to be different in silicate melts also. The partial vapour pressure of any trace element in a magma, being dependent of the bonding properties (chemical forces), will consequently vary with the amount of network formation in the magma. As any distribution coefficient is a function of the partial vapour pressures of the trace element in the two phases concerned it follows that the distribution factors $\left(\frac{\text{conc. in mineral}}{\text{conc. in magma}}\right)$ will, generally speaking, vary with changing composition of the magma.

The partial vapour pressure of a trace element in a mineral is independent of the properties of the surrounding magma with which the mineral is in equilibrium. It would therefore appear that the distribution coefficients governing the distribution of trace elements between two minerals are independent of the composition of the magma. This is true only for minerals of constant composition. Most rock forming minerals are, however, members of an isomorphous series (olivines, pyroxenes, amphiboles, feldspars), and we have no reason to believe that the partial vapour pressure of a trace element in for example albite should be identical to the partial vapour pressure of that element in anorthite. As the composition of minerals belonging to an isomorphous series varies with the composition of the magma, we will also in general expect a variation in the mineral-mineral distribution coefficients with varying composition of the magma.

The distribution coefficients will no doubt vary with pressure also. It is believed, however, that this variation will be unimportant compared to the variation with temperature, and it will not be discussed in this paper.

In an extensive study, Wager and Mitchell (1951) have investigated the concentration of trace elements in rocks of the Skaergaard intrusive complex, and have, for varying stages of crystallization, calculated the distribution factors of a number of trace elements for the minerals plagioclase, pyroxene, olivine, ilmenite, and magnetite (*loc. cit.*, pp. 154–155). In some cases the distribution factors are approximately constant within the limits of error throughout the whole history of crystallization of the magma, as is the case for nickel and cobalt. In other cases there is a marked variation. For example, the distribution factor of vanadium in plagioclase changes from $<0{\cdot}03$ to $8{\cdot}0$, a factor of more than 300. (Thus, at an early stage of solidification of the magma, crystallization of plagioclase

will enrich the magma in vanadium, while at later stages the magma will be impoverished in vanadium by the crystallization of plagioclase.) In general, the variation of the distribution factors in the Skaergaard intrusive complex is in accord with the views expressed in this paper.

A calculation has also been made of the variation in the trace element content of successive residual magmas formed during differentiation of the Skaergaard intrusion (Wager and Mitchell, 1951, p. 176, Fig. 7). It is of the greatest interest to note that their experimentally determined curves have the same general trend as the theoretically calculated curves of Figs. 2–6 in the present paper.

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Potassium feldspars structurally intermediate between microcline and sanidine

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ABSTRACT

Natural K-feldspars exhibiting all states that are structurally intermediate between sanidine (monoclinic) and microcline (with maximum triclinicity) are described. Data based on X-ray measurements are given for selected materials from a variety of geological occurrences. The possible modes of genesis of these triclinic K-feldspars are discussed. The relation of "orthoclase" to sanidine and microcline is also considered. The difficulty of using information on the polymorphism of $KAlSi_3O_8$ in geologic thermometry is pointed out.

Introduction

In a paper dealing with the microcline-sanidine stability relations, the writers (Goldsmith and Laves, 1954) described the production of potassium feldspars (by dry heat treatment of natural microclines) that showed lattice geometry intermediate between that characteristic of triclinic microcline and monoclinic sanidine. All states intermediate between the two structural types could be produced. It is necessary to heat microcline at temperatures above ca. 1000°C to produce these states in a reasonable length of time, and it was pointed out that at temperatures this high, microcline and the intermediate states produced are not stable but exist in a superheated state. The intermediate geometry was attributed to intermediate degrees of Al-Si order-disorder. Natural K-rich feldspars with intermediate geometry were but briefly mentioned in the paper above noted, and will be described here.

Natural Intermediate K-Feldspars

Natural K-feldspars with triclinic geometry (triclinicity) intermediate between that of monoclinic feldspar and microcline[1] are not uncommon. A complete gradation exists between monoclinic material and microcline with maximum triclinicity. This fact necessitates a clarification of the term microcline. It is proposed that the name apply to any of the intermediate K-feldspars that are measurably triclinic, i.e., in which α and γ, and therefore α^* and γ^* deviate measurably from 90°. Triclinic adularia, for example (Laves, 1950, 1952; Chaisson, 1950) is considered as an intermediate microcline with a low Δ-value.[2]

The writers have taken X-ray diffraction photographs of well over 100 selected specimens of potassium-rich feldspars. Those chosen for X-ray work were to some

(1) Microcline showing maximum triclinicity, i.e., ideally a fully ordered K-feldspar. $\Delta = 1$, $\alpha^* \sim 90°25'$, $\gamma^* \sim 92°20'$. Intermediate feldspars have been independently observed by W. S. MacKenzie (personal communication) and their existence is implied by the optical work of G. M. Paraskevopoulos (1953).

(2) The angular deviations of α^* and γ^* from 90° in microcline of maximum triclinicity (see footnote 1) are small enough so that there is a linear relation between Δ, where $\Delta = 12{\cdot}5(d_{(131)} - d_{(1\bar{3}1)})$, and the angular deviations from 90°. Thus a Δ-value gives the direct fractional deviation of the angles α^* and γ^* in terms of a microcline with the geometry given in footnote 1. For example, a Δ of 0·80 would be representative of a microcline with an α^* that is 80% of the way between 90° and 90°25′, and a γ^* 80% of the way between 90° and 92°20′. In the computation of this relationship the a, b, and c axes were considered as being unaffected by a change in triclinicity, and the angle β^* was considered constant. Although the axes are affected by triclinicity change, they have an insignificant effect on the value of Δ.

extent pre-selected as those most likely to show intermediate geometry on the basis of somewhat cursory optical examination or because of an uncommon occurrence. Many samples that appeared to be "normal" high-Δ microclines, or typically monoclinic sanidines were not examined by X-ray means. The best examples of the intermediate materials found are listed in Table 1. This listing is indicative of the fact that a great variety of rock types may contain K-feldspar of all degrees of triclinicity.

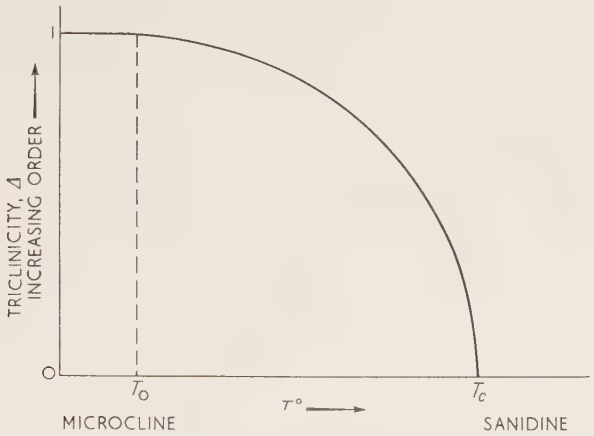


Fig. 1. Diagrammatic representation of the disorder-temperature relations in potassium feldspars.

Before further describing and discussing the significance of these samples, let us consider the theoretically possible ways that microclines may be produced in nature.

Discussion of the conditions for the production of natural intermediate microclines

Fig. 1 is a diagrammatic state-temperature diagram for $KAlSi_3O_8$ as discussed by the writers (1954). Microcline, with maximum triclinicity, is considered to be ordered with respect to Al and Si, and is stable below T_0. Sanidine (monoclinic, triclinicity $= 0$) is considered to be disordered with respect to Al and Si, and is stable above T_c. The states with intermediate degrees of order and with intermediate values of triclinicity, are considered to be stable between T_0 and T_c. The range of temperature between T_0 and T_c is unknown. In the paper above mentioned it was shown, however, that the temperature T_c may be as low as 500°C.

Let us consider a number of ways in which $KAlSi_3O_8$ may crystallize, either from a disperse state, or by recrystallization of pre-existing material.

1. Crystallization above T_c

(a) Sanidine, stably crystallized above T_c, may cool very slowly, and under optimum conditions be continuously changed (equilibrium cooling) to microcline. In so doing it will go through the continuous changes ("transformation path") as illustrated by the arrows of Fig. 2.

(b) Sanidine, stably crystallized above T_c, may cool into the microcline

stability field without change. This is represented by the arrows in Fig. 3, and results in the metastable preservation of sanidine.

(c) Sanidine, stably crystallized above T_c, may in cooling show some tendency to develop an ordered Al-Si arrangement, but without reaching true equilibrium. An infinity of "paths" are possible, a few of which are indicated in Figs. 4a,b,c. These may represent all gradations between (a) and (b) above, and will result in the development of intermediate structural states. These intermediate microclines are, of course, not stable under these conditions of formation.

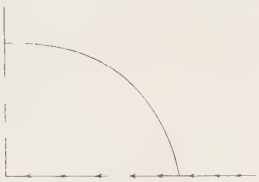


Fig. 2.

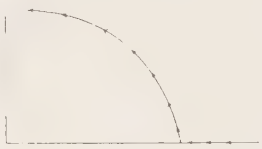


Fig. 3.

Fig. 4a.

Fig. 4b.

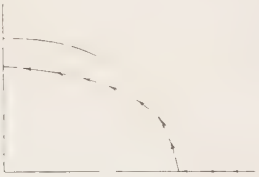


Fig. 4c.

Fig. 5a.

Fig. 5b.

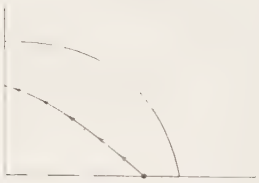


Fig. 5c.

2. Crystallization below T_c

(a) Crystallization of monoclinic K-feldspar (sanidine) may take place metastably below T_c. This is always observed in hydrothermal crystallizations in the laboratory. The possible general paths and end products are diagrammatically shown in Figs. 5a,b,c. In Fig. 5a highly ordered microcline is ultimately produced; in Fig. 5b the metastably crystallized sanidine is metastably preserved; in Fig. 5c an intermediate microcline is metastably produced from the metastable sanidine.

(b) Direct crystallization of an intermediate state may take place below T_c. With equilibrium cooling highly ordered microcline is ultimately produced, as shown in Fig. 6a. Various non-equilibrium paths may be followed with the production of a variety of metastable intermediate microclines, as indicated in Fig. 6b. The remaining possibilities are illustrated in Figs. 7a,b,c, which also represent special cases of an infinity of paths emanating from any point in the diagram.

The production of intermediate microclines or of sanidine by re-heating pre-existing K-feldspar is possible. For example, the earlier mentioned conversion of high-Δ microcline, by a process of superheating, through intermediate states and ultimately to sanidine can be diagrammatically illustrated by Fig. 8. This process can also take place in nature, and might be modified in this case as shown by Fig. 9. It is also possible to produce an intermediate state (or a highly ordered microcline, under the proper conditions) in nature from a pre-existing sanidine by metamorphic re-heating. This could take place as illustrated in Fig. 10; it has not been done in the laboratory.

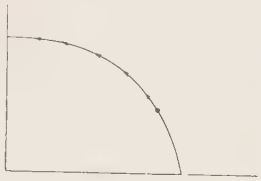


Fig. 6a.

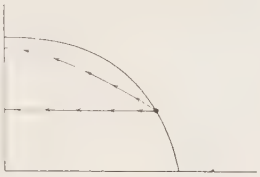


Fig. 6b.

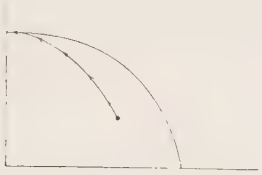


Fig. 7a.

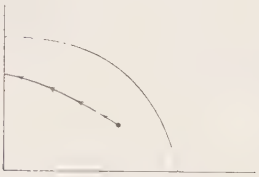


Fig. 7b.

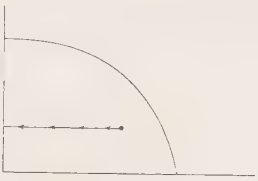


Fig. 7c.

Fig. 8.

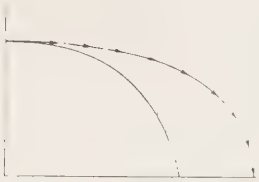


Fig. 9.

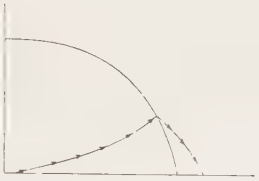


Fig. 10.

It must be realized that all of these paths are purely diagrammatic, and that their configuration would be strongly influenced by the cooling or heating rates. Of Figs. 2–10, only Figs. 2 and 6a represent equilibrium conditions over the whole history of the crystal. In Figs. 5a and 7a equilibrium is ultimately reached. All other paths represent "quenches," of varying degrees of effectiveness. Figs. 8–10 represent superheating.

It is possible that highly ordered microcline, intermediate microclines, or sanidine may crystallize directly under certain conditions at or near earth surface temperatures. This can be considered as taking place at temperatures below those illustrated by the above diagrams, but in the stability field of fully ordered microcline.

Twinning

Microclines can be either single-crystals, polysynthetically twinned after the albite or the pericline law, or polysynthetically twinned after *both* the albite and

pericline laws[3]. By far the most common is the combination albite and pericline twinning, the typical microcline cross-hatching. Laves (1950) showed that the typical cross-hatch twinning[4] is a logical consequence of an inversion from a pre-existing monoclinic single crystal, and could not have been developed as growth twinning. This indicates that the great majority of microclines were originally monoclinic. The reverse conclusion, that untwinned microcline (or microcline twinned only after the albite or the pericline law) is indicative of original triclinic growth is not valid, although it may be highly probable in certain cases. If the original growth was as a triclinic material however, it *cannot* show the typical cross-hatching.

This genetic view of twinning can be correlated to some extent with the preceding discussion of the ways in which K-feldspar can be crystallized. In all cases where a monoclinic feldspar is first formed (either stably or metastably), cross-hatch twinning might be expected to be developed. Thus cross-hatching would be likely in the cases illustrated by Figs. 2, 4, 5a, 5c, and (all but in the final product of) Fig. 10. Although crystals that have been developed in any one of these ways *need* not be cross-hatched, if crystals *are* found to be cross-hatched, they can be said to have been produced by one of these mechanisms. The presence of cross-hatch twinning in a K-feldspar excludes the formational mechanisms illustrated by Figs. 6 and 7.

Discussion of specimens

A single morphological unit[5] of K-feldspar may show a large variation in triclinicity from spot to spot. Most K-feldspars that have been examined showed either monoclinic (or nearly monoclinic) symmetry, or maximum or nearly maximum triclinicity, and are quite uniform in this respect from spot to spot in the same morphological unit. Those feldspars that show intermediate triclinicity tend to show variation in triclinicity from spot to spot.

Pegmatitic feldspars. An example of the above variation is seen in sample No. 1 (pegmatite, Tammela, Finland) of Table 1; here are shown 4 values of triclinicity ranging from 0·58 to 0·94. These values were measured from 4 tiny fragments (each sample several milligrams or less, crushed for powder diffraction photographs) taken from 4 different places from a cleavage piece of pegmatitic feldspar approximately 2 inches in all dimensions.

Sample No. 2 (pegmatite (?), Jekaterinburg, Urals) is quite interesting, and shows the greater part of the complete triclinicity range over very small distances within the morphological unit. The specimen is a cleavage piece approximately one inch on a side, and single-crystal diffraction shows that in places the triclinicity passes from 0 to 0·8 in a distance of one millimetre or less. This specimen was

[3] Neglecting rarer types of growth twins.

[4] Where the X-ray evidence shows that four and only four different orientations (A_1 A_2 P_1 P_2) are related to each other such that A_1 A_2 are albite twins and P_1 P_2 are pericline twins, with the twin axis of P_1 P_2 being perpendicular to the twin plane of A_1 A_2

[5] The term "morphological unit" will be used for the most part in place of the more restrictive term "crystal." K-feldspars are commonly perthitic, and thus consist of two phases. In addition the almost universally present twinning further subdivides the "crystal." A morphological unit may thus range from any homogeneous single-crystal to any heterophase, twinned aggregate that is morphologically distinguishable from its surroundings.

Table 1. *Selected K-feldspars with intermediate triclinicity*

Sample No.	*Description*	*Representative Δ-values*	*Comments*
1	Pegmatite, Tammela, Finland	0·58	Green portion of large green and white xl.
		0·79	Another green portion
		0·88	Another green portion
		0·94	White portion
2	Pegmatite (?) Jekaterinburg = Ekaterinburg = Sverdlovsk	0·20 ~0	Variable optical extinction, even in "single-xl." portions
3	Pegmatite, fairly clear perthite, with "glassy" coating	0	Shows cross-hatching, with low but variable extinction angle, yet monoclinic by powder method
4	Pegmatite, locality unknown	(131) region smeared out	~ Entire range of Δ in tiny portion of xl.
5	Granite porphyry, Högland, Finland	0·49 0·68 0·54	Portions of different phenocrysts
6	Granite porphyry, Rehberger Graben, Andreasberg	0·79 and 0	Intermediate microcline plus monoclinic material
7	Granite porphyry, Auvergne, Frankreich	(131) line diffuse	Mostly monoclinic, plus some range of intermediate material
8	Granite porphyry, Klein-Langenberg, Sowen, Vogesen	0·59	
9	Granite porphyry, Sewensee, Vogesen	0·49	
10	Granite porphyry, Erdmansdorf, Schlesien	0·84	
11	"Adularia," near Hot Springs, Arkansas	~0	Tiny crystals, <1 mm
		(131) line broadened	Tip of ½ inch xl.
		(131) quite broad	Fragment of "massive" material
		0·71	Another fragment from "massive" material
12	Chesterlite, Chester Co., Pa.	0·78 and less	Adularia-like habit. Optics variable

Table 1 (*continued*)

Sample No.	*Description*	*Representative Δ-values*	*Comments*
13	Authigenic microcline, Stonehenge limestone, Bellefonte, Pa.	0·83	Sector-twinning (albite law), as in adularia
14	Åvon granite, Finland	0·42 ~0	Portions of 2 different xls. Optical variations within xls. also seen
15	Porphyrytic Rapakivi granite, Pitkäranta, U.S.S.R.	(131) slightly diffuse	
16	Rapakivi, Antrea, Finland	(131) very diffuse	Considerable Δ-range within xls.
17	Green Rapakivi, near Kaipiainen, Finland	(131) somewhat diffuse	
18	Olivine syenite, Laramie Range, Wyo.	(131) somewhat diffuse	
19	Granulite, Ivalojoki, Finland	(131) somewhat broadened	"Flame" microperthite
20	Sillimanite granulite, Finland	(131) quite diffuse	Considerable Δ-range in one xl. Microperthite.
21	Garnet granulite, Mahlattinuora, Finland	~0 to 0·58	Large Δ-range within xl. Microperthite
22	Mylonitic granulite, Koabbilavdshi, Finland	(131) region a broad band	Apparently entire Δ-range represented
23	Banded granulite, Highroad to Sikavuono, Finland	0·88 0	Microperthite, total Na_2O = $3{\cdot}1_5\%$ Another xl., total Na_2O = 3·1%

Specimens are discussed in the text. The above Δ-values were determined by the powder method. Single-crystal data on selected specimens are presented in the text. Accuracy of the Δ-values is approximately ±0·05.

kindly supplied by Prof. O. B. Bøggild, and his optical description (Bøggild, 1924, p. 16) follows:

> "Most of the orthoclase substance consists of a single individuum of microcline, the extinction of which is almost 15°, but where it borders on the broader, more irregular albite lamellae it passes gradually into an orthoclase with parallel extinction. Of the common microcline structure there are only small traces, and the opposite individual is only in a few instances developed independently. The more regularly reflecting albitic lamellae[6] are always situated in the single microcline, and we have here, consequently, the only known instance of labradorizing microcline."

This specimen will be discussed from another point of view in a subsequent paper on the Na_2O content of K-feldspars.

Specimen No. 3 is from the El Molino gem pegmatite mine, Hiriart Hill, Pala, San Diego Co., California, and was collected by Dr. W. T. Schaller. Similar material is described by Jahns and Wright (1951). The specimens examined by the writers consisted of large crystals (up to 6″) of clear but perthitic K-feldspar, many of them showing a "glassy" non-perthitic coating 1–2 mm thick. Both the main portions of the crystals and the coating show triclinic (cross-hatch) extinction on (001) in many places, although most of the material has approximately parallel extinction (although somewhat undulous) against the trace of (010). The largest extinction angles observed are approximately 8–10°, roughly one-half that of "maximum" microcline. The cross-hatching is very poorly developed, and is observed for the most part (as is usual) at the contacts with the well-developed exsolved albite lamellae, but at random where present in the non-perthitic coating. This behaviour is the opposite of that observed in the Jekaterinburg specimen. The development of triclinic material around other obvious areas of imperfection (inclusions, etc.) is also apparent. Fig. 11 is a photomicrograph of this specimen. A single crystal X-ray photograph taken of a fragment of this material adjacent to a "negative crystal" (void, with crystalline outline) showed a γ^* value of approximately 90°55′, indicating a triclinicity of roughly 0·5 (extinction angle was 9°). Nevertheless, powder photographs taken of material from a number of places on these crystals showed only monoclinic symmetry. It is apparent that only a rather small amount of the sample deviates from monoclinic symmetry, an amount insufficient for detection by normal powder methods. This is typical of the results obtained from adularias, even those that show considerable optical deviation from monoclinic symmetry. A very small amount of triclinic material, even of low triclinicity, is detectable optically (particularly if cross-hatching is present), an amount insufficient to show splitting or diffusing of lines when the powder technique is used.

Specimen No. 4 is a large unit (3–4″), well bounded by crystal faces. The locality is unknown, but it is almost certainly from a pegmatite. Powder patterns show that the complete range of triclinicity exists, as expressed by a broad diffuse band in lieu of definite (131) and ($1\bar{3}1$) reflections. Some portions of this (and other specimens) have such a wide and uniform distribution of triclinicity that the (131) and ($1\bar{3}1$) and (130) and ($1\bar{3}0$) etc. reflections are developed as broad diffuse bands

[6] This refers to the "schiller" in this specimen described by Bøggild.

that can barely be perceived above the background. Under the microscope this material shows a variety of cross-hatch twinning, from sharp well-defined twin lamellae all the way to vague and indefinite "single-crystal"-appearing areas with various extinction angles. Here again is seen complete and continuous gradation from monoclinic to triclinic geometry over very small areas and within a "single-crystal" (morphological unit).

Granite porphyries. Sample No. 5 is a granite porphyry from Finland. In Table I three triclinicity values are shown (ranging from 0·49 to 0·68), and were obtained from different portions of a single morphological unit, in this case a 1 cm phenocryst. A single-crystal X-ray photograph of a fragment of a phenocryst shows blurred-out albite and pericline twin reflections indicating a range of triclinicity from a moderate value all the way to monoclinic symmetry. No definite cross-hatch twinning is observable under the microscope, but the material has somewhat wavy extinction.

Sample 6, from another granite porphyry, Andreasberg, shows a mixture of monoclinic material with triclinic material of $\Delta = 0{\cdot}78$. No gradation was observed in the powder photograph of the single sample that was X-rayed.

Several other granite porphyries containing K-feldspars of intermediate triclinicities are also shown in Table 1. Sample 7, from a granite porphyry, Auvergne shows a somewhat diffuse (131) reflection, with the greatest intensity contribution falling in the centre of the reflection, indicating that the material is for the most part monoclinic, but with some material of variable but low triclinicity also present. The writers examined 24 samples of granite porphyry for a particular reason; it was considered not unlikely that some might have crystallized slowly enough at a temperature in the range between T_0 and T_c (Fig. 1) so that a triclinic K-feldspar might have directly crystallized. If so, the crystals should not show the cross-hatch twinning relations. No conclusive evidence for this type of crystallization has as yet been found. The K-feldspars of typical granite porphyries for the most part appear monoclinic when tested by powder diffraction methods.

Adularia-like K-feldspars. Variations in the optical properties within adularia crystals was discussed by Mallard (1876). Köhler (1948) observed a variety of extinction angles in adularias, and described one specimen in which the full extinction angle of microcline was observed. Chaisson (1950) described the triclinic portions present in certain adularias, and concluded (p. 547) that "Triclinic adularia occurs as a secondary modification of monoclinic adularia. It has distinctive optical properties and behaviour which establish it as a variety of potash feldspar." This conclusion is overstated in the light of the variation of the position of the indicatrix as described by Chaisson. The claim for establishment of a "variety" of K-feldspar may have been strengthened by the apparently uniform triclinic geometry observed by Laves (1950) in those most-triclinic portions of the same specimens examined by Chaisson. This view was later modified by Laves (1952), and the present data show that all geometries intermediate between monoclinic and maximum triclinic can be present.

Sample No. 11 was made up of a large number of crystals associated with vein quartz, collected approximately 30 miles west of Hot Springs, Arkansas, by Dr. W. T. Schaller. Some of the material was massive in nature, but well crystallized specimens ranged from microscopic size up to approximately one inch. The habit

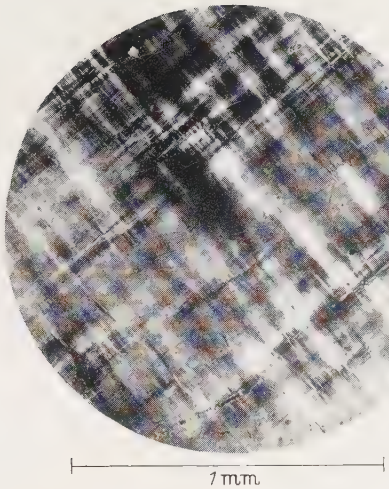


Fig. 11. Photomicrograph of "glassy" nonperthitic coating on specimen No. 13. Section on (001), at surface of crystal. Much of crosshatched material has a very low extinction angle, less than 2 3°. X-ray powder photographs appear monoclinic. Well exposed single-crystal pictures show weak "tails" on certain of the monoclinic reflections, indicating a small amount of material with a varying Δ, > 0. A similar but more pronounced effect is described in Fig. 12 c.

is typically adularia-like, and this feldspar has been described as adularia by Engel (1946) in a report on the Arkansas quartz deposits. The crystals are cloudy, or opaque in bulk, although relatively clear in thin section. Under the microscope the typical sector-appearance of adularias is apparent, as are variations in extinction angle as described by Mallard (1876), Köhler (1948), and Chaisson (1950). No cross-hatch twinning was observed. Spectrographic analysis (by O. Joensuu) showed less than 0·5% Na_2O. X-ray powder photographs taken of different portions of different crystals show triclinicities ranging from 0 to 0.71. In some of the photographs the (131) reflection appears as a broad band, indicating a sizeable range of triclinicity within the small sample used for the X-ray work. Single-crystal photographs show that the triclinic portions are not sub-microscopically twinned, but that small portions of the triclinic sectors act as single crystals. In one case a γ^* value of approximately 91° was found ($\Delta = \sim 0{\cdot}4$).

Sample No. 12, a chesterlite (microcline) from Poorhouse Quarry, Chester County, Pennsylvania, also has typical adularia morphology. The intergrown wedge-shaped crystals are up to one inch in length, and are cloudy or almost opaque in bulk, as in the case of specimen 11. Under the microscope the typical adularia-like sector extinction is seen, with very variable behaviour from place to place. In places cross-hatching is also present; also quite variable in appearance. This material is the most triclinic adularia-like feldspar observed by the writers. Powder patterns showed values of Δ as high as 0·78. Most of the material is definitely triclinic; even portions that had monoclinic extinction on (001) proved to be predominantly triclinic when examined by the single-crystal technique (sub-microscopically twinned so as to produce monoclinic extinction), although some truly monoclinic material was present. This is illustrated and further explained in Fig. 12b. In this particular fragment, approximately 60% is triclinic (with a triclinicity of 0·60) and 40% is monoclinic. This "chesterlite," like adularias in general, is a single phase, with no exsolved albite.

Authigenic K-feldspars. Little will be said here about authigenic K-feldspars, as this subject will be treated in detail in a forthcoming work by Y. Baskin, of the University of Chicago. Baskin (personal communication) has found that most authigenic K-feldspars are monoclinic. Several highly triclinic microclines have been found however, and a number with intermediate triclinicity. Only one sample (No. 13, authigenicm icrocline, Bellefonte, Pa.) with $\Delta = 0{\cdot}83$ is listed in Table 1.

Granitic rocks. The K-feldspars of the relatively small number (approximately 20) of "normal" granites examined for this investigation were for the most part highly triclinic microclines, and less commonly, monoclinic "orthoclase." Several granites from Finland with intermediate K-feldspars are included in Table 1, however.

Specimen No. 14 is a fairly coarse-grained granite (Avon, Finland) with feldspar crystals up to 1/2 inch in size. Several crystals were examined optically, and all gradations from monoclinic through finely cross-hatched to coarsely cross-hatched portions are observable. Where cross-hatched, the amount of material in (+) and (−) twin positions varies considerably so that some areas are virtually "single-

crystal" in nature, and others are well balanced with respect to the two positions. A single-crystal X-ray picture of one of the "single-crystal" areas shows no twinning, and γ^* is $\sim 91°$, indicating a triclinicity of $\sim 0{\cdot}4$. See also Fig. 12c, an X-ray precession picture of another fragment, showing a range of Δ. Two powder photographs taken from two different crystals show values of 0 and 0·42, and other values could undoubtedly be found.

Three rapakivi granites, specimens 15, 16, and 17, are listed in Table 1. All three show diffuse (131) reflections, indicating that a range of triclinicity is present in the tiny fragment used for the X-ray pattern. A total of 16 different specimens of Finnish rapakivi granites (from the several different rapakivi areas) were investigated, and with the exception of the above 3, no triclinic K-feldspar was observed. The typical Finnish rapakivis might thus be said to have K-feldspar that is "monoclinic" (also see ESKOLA, 1951, pp. 40–41). Nearby non-rapakivi-type Finnish granites show either "monoclinic" or highly triclinic K-feldspars, but as appears to be true with granite in general, the triclinic varieties are probably more common. Also in contrast with the Finnish rapakivis are those rocks called rapakivi by EMMONS *et al.* (1953) from the Waupaca, Wisconsin, area. Six samples of Waupaca rapakivi all showed highly triclinic K-feldspars.

Specimen No. 18, an olivine syenite from Wyoming, shows somewhat diffuse (131) reflections in 4 specimens examined, indicating a low but definitely triclinic geometry that might be characteristic of a large body of the rock.

Granulites from Finland. Professor PENTTI ESKOLA kindly sent the writers a suite of granulite facies rocks from Lapland (see ESKOLA, 1952). On p. 148 ESKOLA states, "The first stage of alteration of the clear orthoclase into microcline appears in the form of undulating extinction (Fig. 17). Gradually extremely fine twinning lamellae appear in the most strained parts of the crystals, and finally the whole crystal is cross-hatched microcline (Fig. 18), while other specimens display only well developed quadrille structure." The "microclinization" described by ESKOLA can be shown by X-ray diffraction to go hand-in-hand with variability of triclinicity. The optically undulating, or shadowy areas generally are composed of material with intermediate geometry.

Some of the granulite samples are listed in Table 1, and the whole range of triclinicity is shown. No. 19, from a granulite, Finland, shows slight broadening of the (131) reflection, in No. 20 it is quite diffuse, in Nos. 21 and 22 it is a broad band, and in another portion of No. 20 it is broad enough to represent the entire range of triclinicity (the outer portions of the band representing the (131) and ($1\bar{3}1$) spacings of a microcline with "maximum" triclinicity).

Sample No. 23 contains separable grains of monoclinic and triclinic material. Under the microscope fairly large areas of optically monoclinic feldspar were seen. A triclinicity of 0 was established by powder and single-crystal techniques. Other crystals, as well as other portions of certain crystals were optically highly triclinic and were separable as individuals with extinction on (001) up to $\sim 15°$. A Δ-value of 0·88 is shown in Table 1 for a powder determination on one of these crystals. A single crystal photograph showed $\gamma^* = 92°6'$ ($\Delta = 0{\cdot}90$). The monoclinic and triclinic fragments shown in Table 1 were taken from adjacent crystals, and aside from extinction angle, were identically-appearing micro-perthites.

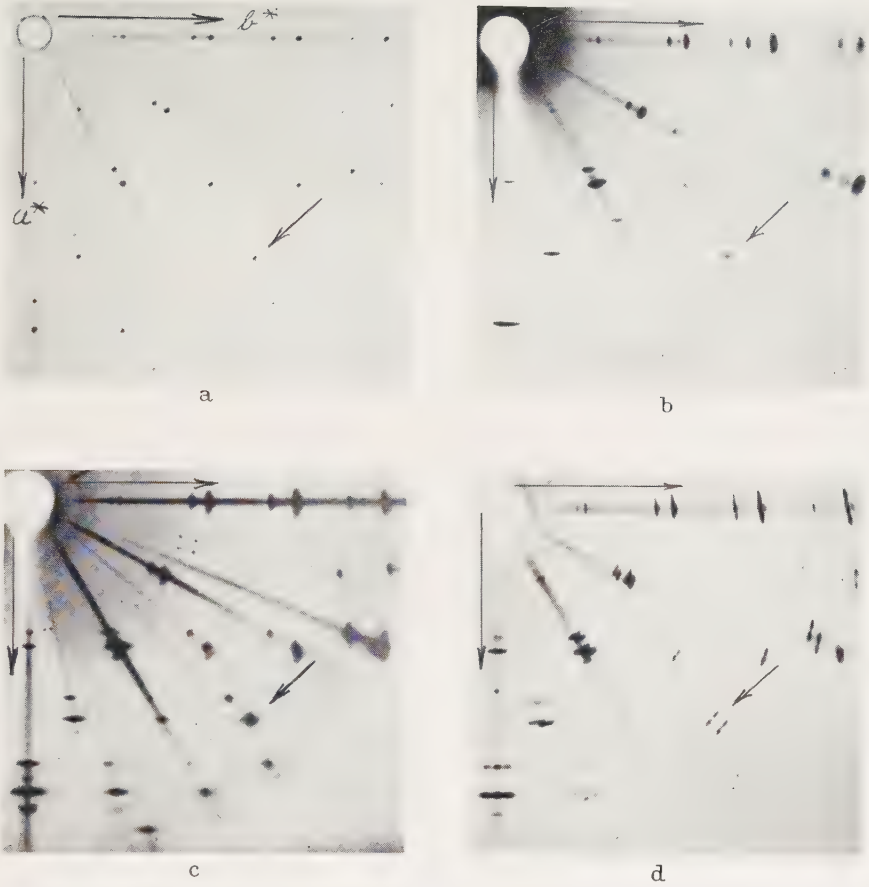


Fig. 12 a–d. X-ray precession photographs, in the c-axis direction. Unfiltered Cu radiation. Diagonal arrows point to areas where characteristic albite-pericline twinning is best shown, the (350), ($3\bar{5}0$) region. Only one quadrant of the picture is reproduced.

(a) Sanidine, only monoclinic reflections present.

(b) Specimen No. 12, chesterlite, intermediate microcline. Monoclinic reflections are present, as are albite-twin reflections from a material with a range of Δ, but most of which is $\sim 0{\cdot}6$. The range of Δ is indicated by the diffuseness of the albite-twin reflections. Some additional reflections due to extraneous radiations are present.

(c) Specimen No. 14, from Avon granite, Finland. The (350) and ($3\bar{5}0$) reflections form a four-fold star, the "rays" of which point toward the corresponding spots of Fig. 12 d. A continuous range of triclinicity is thus shown, with the bulk of the material having a low Δ value. Picture overexposed for purposes of illustration; the specimen was approximately 0·2–0·3 mm in size, as were those of Figs. 12 a, b, and d. Fairly strong reflections from exsolved albite also present, for example the (400) reflection of albite.

(d) Microcline, Hybla, Ontario, with "maximum" triclinicity. Albite-twin and pericline-twin reflections approximately of equal intensity. Reflections from exsolved albite also present.

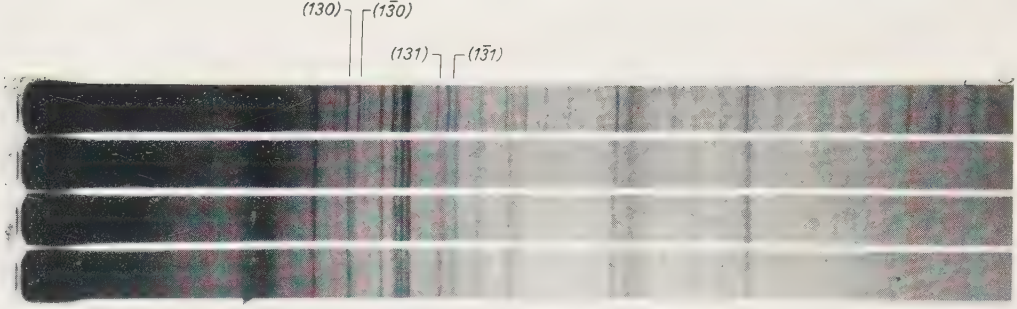
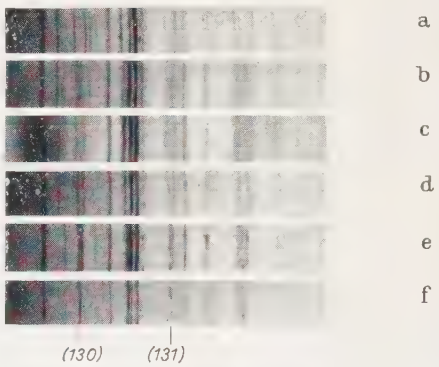


Fig. 13. X-ray powder photographs of a single-phase (authigenic) microcline, illustrating artificially induced intermediate states. Top picture has $\Delta = 0{\cdot}96$. Remaining 3 samples were heated at 1050° C for periods of 10 days, 2 weeks, and 1 month. The bottom picture is of sanidinized material, monoclinic. All four photographs taken simultaneously with quadruple Guinier-type focussing camera (Nonius Co., Delft, Holland). Cobalt radiation, monochromatized with bent quartz crystal. Exposure time 20 hours through powdered sample dusted on 0·001 inch pressure-sensitive polyester film. The (130), (1$\bar{3}$0), (131), and (1$\bar{3}$1) reflections are indicated.

Fig. 14 a–f. Portions of X-ray powder photographs of selected samples. Segments cut from films taken with Guinier-type camera, as in Fig. 13.

(a) Microcline, Tammela, Finland, with $\Delta = 0{\cdot}95$.
(b) Specimen No. 16, Rapakivi, Antrea, Finland. Diffuse (131) and (130) regions show that considerable portion of the triclinicity range is present.
(c) Specimen No. 5, granite porphyry, Hogland, Finland, $\Delta \sim 0{\cdot}7$.
(d) Specimen No. 14, Avon granite, Finland, $\Delta = 0{\cdot}42$.
(e) Specimen No. 2, pegmatite (?), Jekaterinburg, Urals, $\Delta = 0{\cdot}20$.
(f) Orthoclase from Madagascar, $\Delta = 0$.

Various amounts of exsolved albite observable as extraneous lines in all samples but (f).



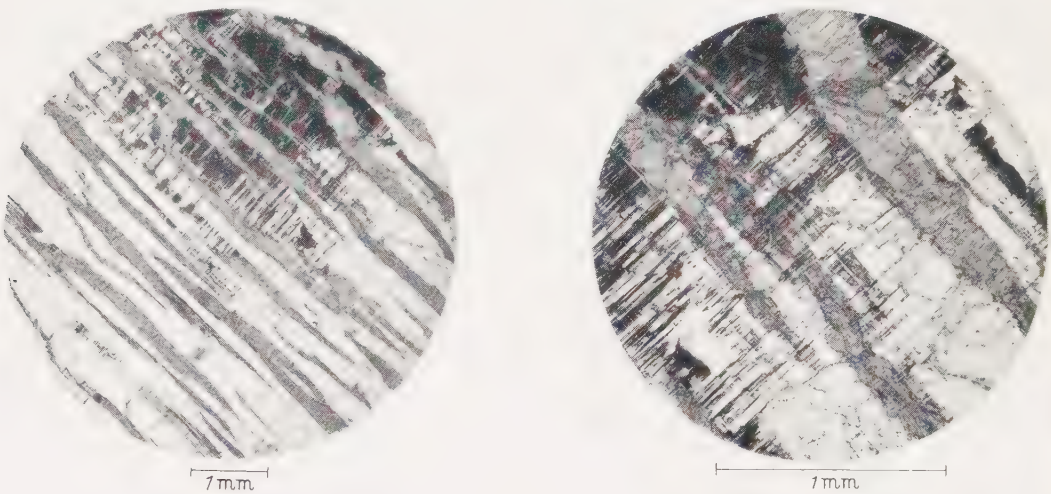


Fig. 15 (a). Photomicrograph of the Pellotsalo microcline. Light areas are the (predominantly) untwinned microcline. Darker grey stringers are albite lamellae. One of the (subordinate) areas of cross-hatching is shown, here grading into albite-twinned microcline, and ultimately into a patch of predominantly "untwinned" microcline in the opposite extinction position.
(b) Enlarged section of (a), showing cross-hatched area.

Spectrographic analysis by O. Joensuu showed the same bulk composition, as follows[7]:

	Na_2O	K_2O	CaO	BaO
Monoclinic portion	3·1	11·5	$1·0_5$	0·3
Triclinic portion	$3·1_5$	11·7	1·0	0·3

The *a*-axis spacings taken from the X-ray photographs shows that virtually all of the $NaAlSi_3O_8$ is exsolved in both portions, i.e., that both have approximately the same, and very little Na in solid solution.

No rocks generally conceded to be metamorphic other than the Finnish granulites were examined.

In Figs. 13 and 14 are shown powder diffraction photographs of several of the K-feldspars, illustrating some of the effects discussed.

Discussion of the Genesis of Triclinic K-Feldspars

The great majority of microclines show the combination albite-pericline cross-hatching with geometric relations such that the twinning can be accounted for by inversion but not by growth. It can therefore be concluded that the great majority of K-feldspars originally crystallized with monoclinic symmetry. *It can not be concluded, however, that the original monoclinic crystallization was a stable one, i.e., that it took place in the stability field of monoclinic K-feldspar.* The strong tendency for feldspars to *metastably* crystallize as the disordered, or high-temperature modification, is discussed by Goldsmith (1953), and can be expected to take place readily below T_c (Fig. 1), in the stability field of microcline. Crystallization of monoclinic K-feldspar does not imply a high temperature of crystallization; this is amply demonstrated in nature and in the laboratory.

The orthoclase-microcline relationship

A brief summary of some of the observed properties of K-feldspars follows:

(1) Most microclines are twinned with four positions that may be designated A_1, A_2, P_1, P_2. A_1 and A_2 are related by the albite law. P_1 and P_2 by the pericline law. As shown by Laves (1950, Figs. 8A and 8B), A_1 and P_1 on the one hand, and A_2 and P_2 on the other have approximately the same orientation (within $\sim 3°$) and therefore similar optical extinction when viewed on (001). A_1 and P_1 material can be called (+) material, and A_2 and P_2 (−) material (corresponding to the (+) and (−) directions of extinction).

(2) The relative amounts of (+) and (−) material (domains) may vary greatly, even from place to place in the same morphological unit.

(3) The size of the (+) and (−) units may vary greatly, and they are observed to be of macroscopic, microscopic, and sub-microscopic dimensions.

(4) The degree of triclinicity has been found to vary from 0 to the maximum observed for microcline (~ 1). Under the assumption that triclinicity is an expression of degree of order, all degrees of order-disorder have been observed in K-feldspars.

[7] Na_2O and K_2O analyses stated accurate to $\pm 5\%$ of the amount present, CaO $\pm 10\%$.

(5) The degree of triclinicity may vary from place to place in a single morphological unit.

(6) If the sizes of the (+) and (−) units are sufficiently small, the degree of order cannot be expected to be expressed in the triclinicity. It has been shown by LAVES (1952, pp. 562 ff.) that the geometry of very small (sub-microscopic) crystalline regions in the feldspars is strongly influenced by the adjacent material. Thus normally monoclinic material may be "forced" to be triclinic and vice-versa. This is analogous to the coherency relations observed in many alloy systems. Thus the (+) and (−) positions, if sufficiently small, may influence the geometry of each other in such fashion that the triclinicity observed by X-ray techniques would be considerably less than would be expected from the degree of order present.

Optically monoclinic orthoclase characteristically shows diffuseness in certain of the reflections in well-exposed single-crystal X-ray photographs (LAVES, 1950). The diffuseness is somewhat variable from sample to sample, and is described in the above reference. This diffuse scattering, not observed in sanidine, is evidence for the existence of the sub-microscopic regions here discussed.

From these observations the following conclusions can be drawn:

(A) If the (+) and (−) regions are equal in amount, and are sub-microscopic, the material will be optically monoclinic. In principle this is similar to MALLARD's hypothesis (MALLARD, 1876). X-ray data may show considerable variability in the triclinicity of material of this nature.

(B) If the (+) and (−) regions are sufficiently small, even if each region is highly ordered with respect to Al and Si, an apparently monoclinic X-ray pattern can result. The relative rates of nucleation of triclinic material within the original monoclinic material and the rate of "growth" of these nuclei determine the size of the regions.

(C) All degrees of Al-Si order may exist within the very small (+) and (−) regions. Thus the material may approach true monoclinic symmetry on this basis. (As the degree of order approaches zero (complete disorder), the regions no longer exist, and a true monoclinic material (sanidine) results.)

(D) K-feldspar that appears monoclinic and that is constituted in one or more of the ways A, B, C described above, is here considered to be what is commonly called orthoclase. The variability in orthoclase, observed both optically and by X-ray diffraction, can be explained by the above model.

(E) On the basis of the above reasoning, earlier statements have been made (LAVES, 1952; GOLDSMITH and LAVES, 1954) to the effect that "orthoclase" is a "group" term and cannot be considered as a unique phase, and that "orthoclase" as such cannot be assigned a well-defined stability field.

(F) Whereas one might normally expect the (+) and (−) regions to be approximately balanced, i.e., equal in amount, this may not always be the case. If either predominates the material will be obviously triclinic. Such sub-microscopic "unbalanced" material was described by LAVES (1950, p. 553) and its existence is indicated by MALLARD's hypothesis (1876). Triclinic K-feldspar, with an optical extinction angle on (001) less than the maximum value for microcline ($\sim 18°$) can

thus be produced in two ways: (a) By "unbalanced" twinned material, and (b) By single-crystal material with an intermediate degree of order. These two effects can, of course, work together in any degree. It is apparent that the ultimate in "unbalanced" material is a single-crystal microcline, with any degree of triclinicity.

Origin of untwinned microcline

There are several mechanisms by which single-crystal[8] microclines may be produced:

(1) By direct crystallization from a disperse system in the stability field of microcline.

(2) By replacement of a pre-existing solid.

(3) By secondary formation from a pre-existing monoclinic K-feldspar.

(a) By a process of solid-state change in which the transformation monoclinic → triclinic begins at one spot (nucleus) and develops from this point throughout the whole morphological unit. (This can be contrasted with the development of orthoclase, where nucleation of "triclinic" (+) and (−) regions (domains) is here considered to have taken place at a great many spots throughout the crystal.)

(b) By first, the development of (+) and (−) domains as discussed above, followed by solid-state domain enlargement. Thus an orthoclase or finely-twinned microcline may ultimately develop into a single domain, i.e., in this case, a single crystal. As in the case of secondary re-crystallization in certain metals, a single domain may grow and engulf the others.

As will be shown, case (1) above, is very rare. The writers are unaware of any example of case (2), but must plead ignorance on this matter. The general mechanism of case (3) is that which the writers believe to be the common one responsible for the production of untwinned microcline. Whether untwinned material is principally developed by mechanism (3a) or (3b) is open to question.

Mäkinen (1913), and more recently Eskola (1951) have described microcline perthite from Finland, with K-feldspar that is predominantly untwinned. Mäkinen and Eskola describe the microcline as "primary," and consider any observable cross-hatching as being secondarily induced in the original triclinic material. Professor Eskola kindly supplied us with a sample of such material from Pellotsalo and this feldspar was investigated both optically and with X-rays. Areas of incipient to well-developed cross-hatching are present in the predominantly single-crystal microcline, a fact also mentioned in the optical descriptions by Mäkinen and Eskola. Fig. 15 is a photomicrograph of one of these areas in the Pellotsalo microcline.

Eskola states (1951, p. 40): "The observations by Mäkinen and myself, however, show that untwinned microcline normally occurs as the primary phase in the potash feldspars of granites and pegmatites, as in the Pellotsalo microcline, and that cross-grating develops in this as well as in the primary orthoclase of rapakivi, etc." On the basis of the optical evidence it is certainly no less likely that the

[8] Growth twins are considered equivalent to single-crystals in this discussion.

untwinned portions and the twinned portions *both* developed from an originally monoclinic single crystal. We believe that mechanisms (3a) or (3b) were operative in the case of this material.

The same might be said of material described by Sauer and Ussing (1890). Large single individuals (although perthitic), some showing baveno twins, are discussed. In their description they also mention the presence of cross-hatching in places within the morphological units, and thus doubt is cast on the "primary" nature of this microcline.

A number of specimens in Table 1, as well as others that show "maximum" triclinicity have untwinned areas of considerable size (1 mm or more).

Triclinic morphology would be excellent evidence for the primary crystallization of microcline. The writers have for some time attempted to find K-feldspar crystals exhibiting triclinic morphology, but without success. The literature on "single-crystal" microclines, with one exception, is not very instructive on the subject of morphology.

The only microcline known to the writers that exhibits triclinic morphology was described by Bøggild (1911, 1953, p. 372). Tiny overgrowths on larger masses of cross-hatched microcline from Ivigtut were measured by Bøggild, and his angular measurements agree very well with the geometry of highly triclinic microcline as determined by X-ray diffraction. There seems to be no question but that these overgrowths are primary microcline, as defined by mechanism (1), above.

The Ivigtut material may be somewhat similar to that from Hunoholmen, Norway. The Hunoholmen material consists of intergrown microcline and albite, the microcline being finely twinned in the central portions of the morphological unit, but it grades outward into rather coarsely twinned material (albite law, lamellae $\sim$1 mm wide) from which single-crystal fragments can be separated. The X-ray data on this microcline are given by Laves (1950).

There are other triclinic K-feldspars that are almost certainly primary. A number of examples of authigenic microclines (of variable triclinicity) are known, and will be described in a forthcoming publication by Mr. Y. Baskin. A good example of an authigenic microcline with very high triclinicity was used by the present writers (Goldsmith and Laves, 1954) in an investigation of the microcline-sanidine stability relations, and has been described by J. P. Perrenoud (1952). In addition, many adularias that show variable triclinicity (especially in the regions near the surface) may have crystallized directly. These adularias, as well as the authigenic microclines all have a sector-type twinning suggestive of growth originating from a higher-symmetry nucleus.

Some remarks on the Na-content of K-feldspars

The assumption has been made (Goldsmith and Laves, 1954) that the triclinicity (Δ) of K-feldspars is a function of Al-Si order-disorder. The use of Δ as a measure of triclinicity (and of order-disorder) was, however, defined for relatively pure K-feldspar. As discussed in footnote 2, Δ was defined in terms of the deviations of α^* and γ^* from 90° in a manner such that these angles are considered to change *proportionately* towards 90° as Δ approaches zero. The spread of the (131) and ($1\bar{3}1$)

reflections is principally a measure of γ^*. The triclinicity cannot in general be used as a measure of triclinic geometry; for example, a sizeable change in α^* may have but little effect on Δ[9].

Any effect of Na-content on the geometry of K-feldspars must be considered from this point of view. Thus one must determine whether or not any of the intermediate Δ-values earlier described are influenced by $NaAlSi_3O_8$ in solid solution in the microcline. The evidence is quite conclusive that triclinic K-feldspars contain but very little (less than 5%) $NaAlSi_3O_8$ in solid solution[10]. This applies to intermediate, as well as fully triclinic material. The method of determining the amount of $NaAlSi_3O_8$ in solid solution involves a measurement of the (400) spacing (a-axis) with a correction for triclinicity, and will be discussed in detail in a forthcoming paper.

The presence (or absence) of Ab in solid solution is not a necessary condition for intermediate triclinicity. This can be shown in 3 ways:

(1) Natural K-feldspars, with negligible Na-contents, exhibit the full range of triclinicity.

(2) All ranges of triclinicity have been induced in a Na-free microcline (by heating above the inversion temperature, Goldsmith and Laves, 1954, and Fig. 13, this paper).

(3) The Na-content of microclines can be brought to a rather high value by heat-treatment of perthitic material. If a moderate amount of albite is put in solid solution by this technique ($\sim$20% or less), Δ is not significantly changed (see also Goldsmith and Laves, 1954).[11]

Little has been known about the actual Na-content (in solid solution) of microclines. It now appears that microclines have for the most part exsolved virtually all of the albite that was originally in solid solution. In our search for microclines containing dissolved $NaAlSi_3O_8$ (for the purpose of evaluating its effect on Δ) the work of G. M. Paraskevopoulos (1953) was noted, after the data presented in this paper were at hand. On p. 209 several microcline-perthites are listed, for which albite contents (in solid solution) of 15–20% are given. These values were tentatively put forth by Paraskevopoulos, based on an optical method of determination. Four samples, including microclines B_3 and B_5 with listed albite contents of 15% and 20%, were kindly furnished to the writers by Professor Burri, in whose care they had been left by Paraskevopoulos. X-ray measurements disclosed that both samples contained but $\sim$3% Ab in solid solution. It is also of interest that the other two samples examined (A_2 and 0_3, listed as orthoclase-perthites)

[9] It should be realized that in the general triclinic case, lattice-geometry and symmetry must be distinguished. This point has been stressed by J. D. H. and H. G. Donnay (oral communication), who point out that there are numerous substances with triclinic symmetry but with a translation lattice that by chance shows α and $\gamma = 90°$.

[10] The only exception observed by the writers is the material of Sample 2 (Table 1), which shows approximately 15% albite in solid solution. As earlier described, this material appears to be unique from other points of view, particularly in that it shows schiller structure.

[11] It should be pointed out, however, that Δ can be changed by putting in additional $NaAlSi_3O_8$. These data, to be described in a forthcoming publication, involve a change in Δ that is consequent upon the development of a solid solution (apparently metastable) between microcline and albite. Under these circumstances, Δ cannot be used as a measure of triclinicity as earlier defined.

were intermediate microclines. Sample A_2 showed a range of Δ, from zero to some intermediate value, a fact that checks well with Paraskevopoulos' statement that this "orthoclase-like" material shows a variable extinction angle on (001). Sample θ_3 is an excellent intermediate material, with sharp (131) and ($1\bar{3}1$) reflections, and a Δ-value of 0·4.

Summary and Conclusions

In addition to monoclinic sanidine and triclinic microcline with maximum triclinicity (with $\alpha \sim 90°14'$, $\alpha^* \sim 90°25'$, and $\gamma \sim 87°40'$, $\gamma^* \sim 92°20'$), there are, in nature, triclinic K-feldspars with all gradations of intermediate geometry. The deviation from 90° of α^* *and* γ^* (or α *and* γ) of these intermediate microclines can be expressed as the triclinicity. Triclinicity (Δ), for convenience of description is set from 0 to 1, where monoclinic K-feldspar has $\Delta = 0$, and "maximum" microcline has $\Delta = 1$. The continuous range of this triclinicity is assumed to be a function of Al-Si order-disorder. K-feldspars with intermediate triclinicity are not uncommon, and examples from a variety of occurrences are given. Large variations in triclinicity are observed within the same "crystal." A characteristic combination albite-pericline twinning is present in most triclinic microclines, including those of intermediate Δ. This characteristic twinning is indicative of inversion from an original monoclinic crystal. True single-crystal microclines are rare, and most of the so-called single-crystal microclines probably also originally crystallized with monoclinic symmetry. Several exceptions are noted, however.

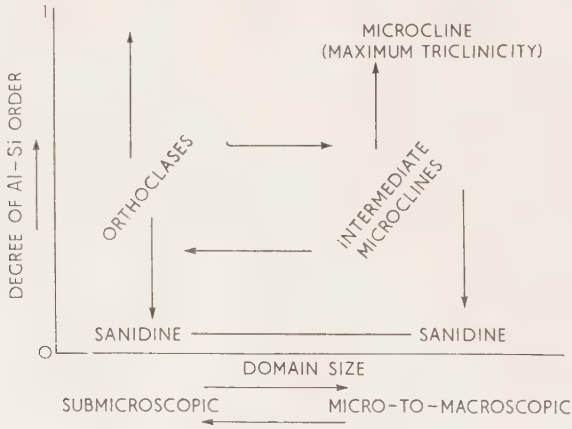


Fig. 16. Diagrammatic representation of K-feldspar relations.

K-feldspars may be composed of triclinic units of any size, as expressed by macroscopic through sub-microscopic twinning. These units or domains are observed to vary greatly in size even within a "single" crystal. Thus, K-feldspars may be continuously variable in *two* ways. (1) degree of triclinicity (an expression of Al-Si order-disorder) and (2) size of these domains (that may show variable triclinicity). It is suggested that as these units become very small, even although each may be highly ordered, the triclinicity is effected by virtue of mutual

stress-strain relations; such material may be monoclinic optically, and even appear to be monoclinic to X-ray powder diffraction or "normally exposed" single-crystal photographs. The writers believe that orthoclase, as opposed to the truly monoclinic sanidine, is constituted in the above fashion; it may thus consist of very small domains (that may be variable in size), and the domains may vary in degree of order. Fig. 16 is a schematic diagram illustrating this conception.

The lowest energy configuration of K-feldspar at or near earth-surface temperatures is a single-crystal microcline, of "maximum" triclinicity. If the material is twinned, it is of higher energy, principally due to strain energy. This (unevaluated) increase in energy might be considerable for material with very small domains. Despite this fact, finely-twinned microclines persist in nature, as do orthoclases, and single-crystal microclines are the exception rather than the rule. It has been shown that the microcline sanidine inversion itself is very sluggish indeed, and to further reduce the total energy by re-organizing the material into single-crystal or even coarsely-aggregated units is exceedingly difficult. Most K-feldspars with intermediate triclinicity show a variation of intermediate geometry from spot to spot, further illustrating the difficulty of attaining equilibrium. It is also apparent that K-feldspar virtually always crystallizes initially with monoclinic symmetry, irrespective of whether it does so in the stability field of microcline or sanidine. It would appear that if crystallization takes place below T_c the stable polymorphic form of K-feldspar is but seldom in equilibrium with its surroundings at the time of crystallization. These considerations may in most cases nullify the use of information on the stability relations of the K-feldspars for the estimation of geologic temperatures.

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The lognormal distribution of the elements: a discussion

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In a recent article in this Journal, Ahrens (1954) proposes a fundamental geochemical law and a powerful corollary of this law. The corollary is clearly a consequence of arithmetic rather than geochemistry, but is not a unique deduction from the law. Even with proper analysis, the data are quite possibly insufficient to establish the law. The analysis provided by Ahrens is thoroughly inadequate.

The law is that ". . . the concentration of an element is lognormally distributed in a specific igneous rock." It is first argued that the concentrations as measured are positively skewed. While this seems almost impossible for major elements in crystalline rocks, it is almost certainly true for trace and minor elements. It is a commonplace that extreme concentrations of such elements are rare but not unknown even in the small samples at our disposal, and it is obvious that the distribution of any element must have a lower bound at zero. The situation is thus ideal for the development of a truncated distribution with positive skew. (This, incidentally, is sufficient to establish the corollary.) Ahrens shows graphically that in his samples skewness is reduced or eliminated by the logarithmic transformation, but similar results might have been obtained with other transformations, so this is not in itself critical with regard to the question of lognormality. It is at most an indication that for certain purposes it might be preferable to use some one of a large family of transformations, all having in common the property of condensing the range of the "raw" observations by reducing large values more than small ones.

Sceptical readers may like to plot a histogram of the cube roots of the Pb values of Canadian granites, given in Table 1 of Ahrens' article. If the base of the first class is set at 0·97 and a class interval of 0·5 is used, the result is an array quite as symmetrical as Ahrens' Fig. 17. This does not demonstrate that the distribution of Pb in Canadian granites is cube-root normal any more than Fig. 17 shows it to be lognormal.

For the purpose of estimating or comparing goodness of fit the class width ought to be much smaller than the standard deviation, maximum values prescribed in standard texts ranging from one-quarter to one-half. In the twenty diagrams presented by Ahrens, class widths are without exception more than half as large as the relevant standard deviations posted in his Table 2; thirteen are larger than 0·75 λ, and seven actually exceed λ in size. A scaling so coarse is incapable of revealing anything of importance about the agreement or disagreement between sample and theoretical distributions. Even a crude test by this procedure would require far more data, and it is largely for this reason that the method has fallen into disuse.

It is disappointing to find that a field in which so much practical progress has

been made in recent years is still content with slipshod applications of interpretative procedures more than a quarter of a century out of date. The Gaddum reference cited by Ahrens contains a careful review of modern methods now widely used for investigating the very question posed by Ahrens. There is no justification whatever for asking readers to rely on an *ad hominem* argument about the matter. This is all they have been offered, and it is to be hoped they will not accept it.

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The lognormal distribution of the elements (2)

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ABSTRACT

More examples of distributions which closely approach lognormality are given and the suggested lognormal law is discussed further, in order to convey more accurately the sense and spirit with which it has been proposed. The magnitude of distortion which can arise when predictions and comparisons are made on the basis of assumed *normal* distribution is illustrated by two examples. Attention is drawn to the significance of the magnitude of the dispersion of concentration for making abundance estimates; Ga (small dispersion), Zr (moderate dispersion), and Cr (extreme dispersion) in granite, serve as examples. An examination of the relationship between the ratio $\frac{\text{arithmetic mean}}{\text{geometric mean}}$ and the magnitude of dispersion of concentration shows that observation accords satisfactorily with theory.

Introduction

The statistical nature of the distribution of the concentration of several elements in some specific geological materials, notably granite, diabase, and muscovite (tin only), was discussed in a previous communication (Ahrens, 1954). The principal conclusion was that distribution was not normal, but of a lognormal type. Two papers on the application of statistics to geochemistry have since been published; the first by Shaw and Bankier (1954), is fairly general, whereas the second (Chayes, 1954) is more specific and criticizes the main conclusion of lognormality arrived at by Ahrens (1954). In the present paper, further examples of a lognormal type are considered and some of the items referred to in the above two papers are discussed as well as a few others which are relevant to the application of statistics in geochemistry.

Comments on the Paper by Shaw and Bankier (1954)

Shaw and Bankier (1954) have recently emphasized the fruitfulness with which statistics can be applied to geochemistry and rightfully point out in their conclusions that progress in quantitative geochemistry is likely to be held up until statistical methods come into more general use. These authors discussed in some detail three main topics—sampling, analytical accuracy, and comparing data. Comparisons of data were, however, based on an assumed normal distribution (the results of Ahrens (1954) had not appeared at the time they wrote their paper), and although such an assumption does not lead to inaccuracy, provided dispersion is small ($C = < \sim 15$–20%), distortion becomes progressively greater with an increase in dispersion and may even lead to the prediction of unreal (negative) concentrations. Two examples will serve to illustrate this point: the first, that of Rb in Ontario diabase (after Fairbairn *et al.*, 1953), which was used by Shaw and Bankier (1954) as one of their examples, and the second that of Sn in muscovite (Ahrens and Liebenberg, 1950).

For Rb in Ontario diabase (excluding Nipigon rocks), am (arithmetic mean) 144 ppm and $s = 86$ ppm ($2s = 172$ ppm), and on the basis of assumed normal

* For earlier observations on igneous rocks as a whole, see Richardson and Sneesby (1922).

distribution, Shaw and Bankier predict that two-thirds of the diabase specimens should contain 58 to 230 ppm Rb (am $\pm$86 ppm), and that the 95 per cent limits are -28 ppm* and 316 ppm (am $\pm$172 ppm): the 95 per cent lower limit is thus negative and unreal. On the basis of assumed lognormal distribution, the most frequent concentration, as indicated by the geometric mean (gm), is 115 ppm $\left(\frac{\text{am}}{\text{gm}} = 1.25\right)$ and the two-thirds limits, 59 and 224 ppm; these are close to those obtained on the basis of assumed normal distribution. The 95 per cent limits are,

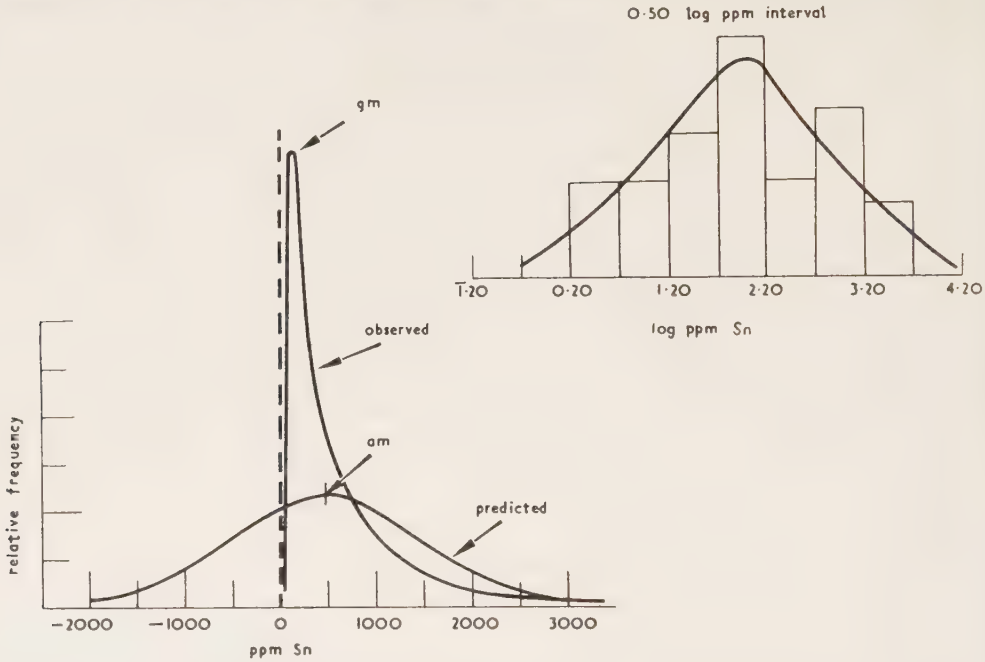

Fig. 1. Slightly idealized observed distribution (– – – – –) of SnO_2 in thirty-eight specimens of muscovite, and predicted distribution (————) based on an assumed normal distribution. The number of observations is small and the comparison is not regarded as fully quantitative; nevertheless it serves to indicate the gross distortion of prediction which arises when dispersion is extreme and normal distribution is assumed. Compare histogram with log SnO_2 as variate.

however, 20 and 440 ppm: these differ distinctly from those predicted on the basis of assumed normal distribution and accord satisfactorily with observation. Dispersion in this example is moderate, but not extreme ($C = 60\%$, $\lambda = 0{\cdot}29$, and $\lambda' = 2{\cdot}0$); in other words, about two-thirds of all samples contain $\times\frac{1}{2}$ to $\times 2$ of 115 ppm Rb. In the example of tin in mica, dispersion is extreme and $\lambda' = \times 8$; that is, $\times 4$ greater than that of Rb (C calculates at about 200%). Two-thirds of all muscovite samples are therefore predicted to contain $\times\frac{1}{8}$ to $\times 8$ of the most prevalent concentration of $\sim$100 ppm; the 95 per cent limits are predicted as $\times\frac{1}{64}$ to $\times 64$ of 100 ppm. The arithmetic mean of tin in mica is 500 ppm; s calculates at 1000 ppm, and normal law would predict the two-thirds and 95 per cent limits as -500 ppm and 1500 ppm, and -1500 ppm and 2500 ppm.

* Shaw and Bankier gave this limit as 0 ppm.

respectively. Even the two-thirds lower limit is negative, and prediction based on assumed normal distribution is grossly distorted in this extreme example. This is illustrated graphically in Fig. 1, which compares a distribution curve based on observation (curve with positive skewness—slightly idealized) with one constructed on the basis of the normal law, using am = 500 ppm and s = 1000 ppm. A histogram (Ahrens, 1954) with log Sn as variate is shown for comparison.

Comments on the Paper by Chayes (1954)

The conclusion of lognormality arrived at by Ahrens (1954) has been criticized by Chayes (1954), partly because the statistical handling of the data is regarded

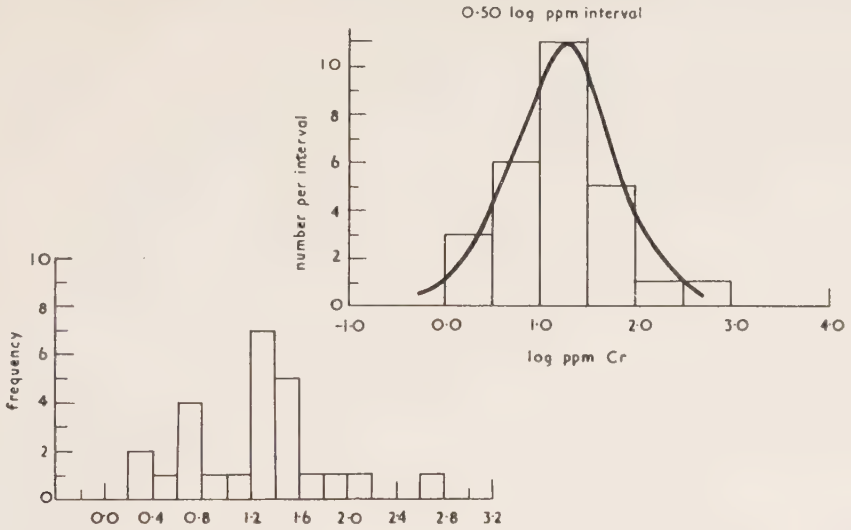

Fig. 2. Histogram of log Cr in Canadian granite, using a class widths of 0·20 (approximately $\lambda/3$) and 0·50.

as inadequate. In a discussion on class width, Chayes draws attention to the recommendation in standard texts that for testing goodness of fit, values greater than one-quarter to one-half of the standard deviation should not be used: the conclusion is then made that the values used by Ahrens are so large (usually 0·75 to somewhat greater than one standard deviation) that they are incapable of revealing anything of importance about agreement or disagreement between sample and theoretical distribution.

Two items will be borne in mind when considering the criticism of the handling of the statistical data; first, that the number of observations per element is small (usually 30–70 determinations: this has been stressed before), and second, that there is a fairly large number of sets of such observations (several elements) and that this fact has influenced the general conclusion of lognormality (Ahrens, 1954). It is generally agreed that a small interval should be used in order to test goodness of fit with high precision, but unless a large number of observations is available this is not possible and a coarser interval must be used. This is illustrated in Fig. 2, which shows histograms for log Cr in Canadian granite using a class

widths of 0·20 ($\frac{1}{3}$ λ) and 0·50. Whereas very little is revealed by the interval of 0·20, the use of a coarser interval of 0·50 (after Ahrens, 1954) is at least able to reveal that the sample distribution is fairly symmetrical and bell-shaped and that to a good first approximation could be regarded as lognormal (the untransformed data show extreme positive skewness). A fairly* critical* test of goodness of fit can, however, also be made despite what has been written in some of the standard texts. Fig. 3, a histogram for Rb in biotite (see discussion below) from igneous rocks may serve as an example. A fairly coarse class interval of 0·20, that is, 0·85 λ, has been used. The fitted curve has been constructed on the basis of assumed lognormality, using the observed parameters of $\lambda = 0{\cdot}235$ and am (logs) = 1·97, and a class

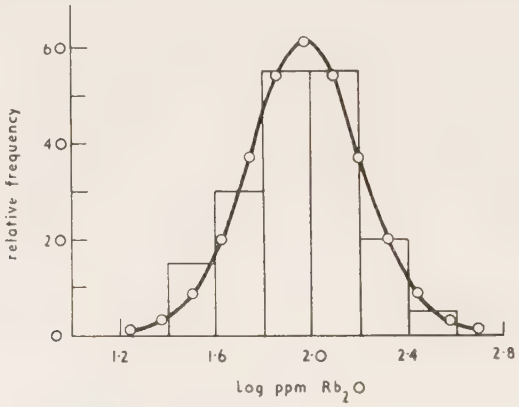

Fig. 3. Histogram of log Rb_2O in biotite with fitted curve (see text).

width of $\frac{1}{2}$ λ. It is evident that fit is close, that to all intents and purposes the distribution of this particular series of observations is very closely lognormal, and that the use of a smaller class width is not likely to alter this conclusion significantly. It must be emphasized that we are not aiming to achieve mathematical purity: such factors as sampling, specificity of geological materials, geographical distribution, implications of the term "granite," degree of alteration, and so on, are such that we never expect exact fit between these observations and one of the type distributions (such as the one in question) set up by mathematicians; in fact, observation rarely ever shows exact fit. Indeed, if an example of perfect lognormality were found, too much emphasis could not be placed on it because of the various factors outlined above which might introduce compensation; hence, the approach has been to place considerable emphasis on the observations as a whole (Ahrens, 1954; see also comments below on Fig. 11 in this respect). We seek to find a distribution which fits the various sets of observation (several elements) reasonably well and which may therefore be used for the geochemical purpose of comparison and prediction. The lognormal distribution fits all sets of observations examined thus far reasonably well, and this conclusion has been

* These are, of course, relative terms, as are also Chayes' statements, "thoroughly inadequate," "slipshod," and "crude," and we shall have to accept the difficulty which arises from different connotations associated with such terms.

expressed in the form of a geochemical law; but, in so doing, it is not meant to imply that exact fit is to be expected in any particular case, that some other distribution might sometimes show slightly better fit, or that on very rare occasions a really serious exception will be found. The original decision to express the general conclusion of close approximation to lognormality in the form of a law was largely influenced by GOLDSCHMIDT's definition of one of the principal tasks of geochemistry, namely, "to find the laws of distribution of the elements." It is highly unlikely that an experienced geochemist such as GOLDSCHMIDT ever conceived

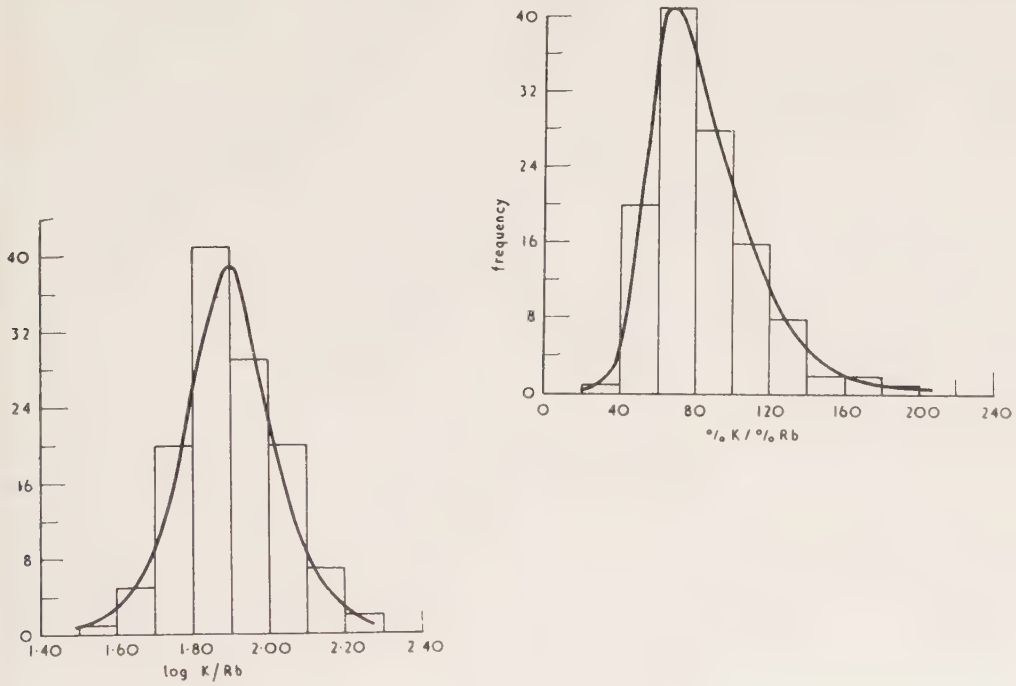

Fig. 4. Histograms for K/Rb and log K/Rb in common igneous rocks and chondrites.

of the possibility of finding any exact geochemical laws—as compared with some of the laws of physics—and the lognormal law was proposed in this spirit.

FURTHER EXAMPLES OF DISTRIBUTIONS WHICH CLOSELY APPROACH LOGNORMALITY

The ratio K/Rb and the ratio Rb/Tl

The close association of K and Rb in common igneous rocks and chondrites (118 observations), and that of Rb and Tl in potassium minerals (165 observations), has been noted (AHRENS, PINSON, and KEARNS, 1952; and AHRENS, 1948, respectively). Histograms using K/Rb and log K/Rb as variates are shown in Fig. 4; that of K/Rb shows slight positive skewness whereas that of log K/Rb

is typically bell-shaped and symmetrical. Greater positive skewness in the K/Rb curve is not anticipitated because dispersion is small and C, λ, and λ' calculate at 33 per cent, 0·14, and 1·4, respectively; $\frac{am}{gm} = 1{\cdot}06$.

Positive skewness is marked in the distribution curve for Rb/Tl in potassium minerals (Fig. 5), and although the geochemical coherence of this pair is considered as close (Ahrens, 1948; Rankama, 1949) it is not nearly as well developed as that of K and Rb in the common igneous rocks and meteorites and λ and λ'

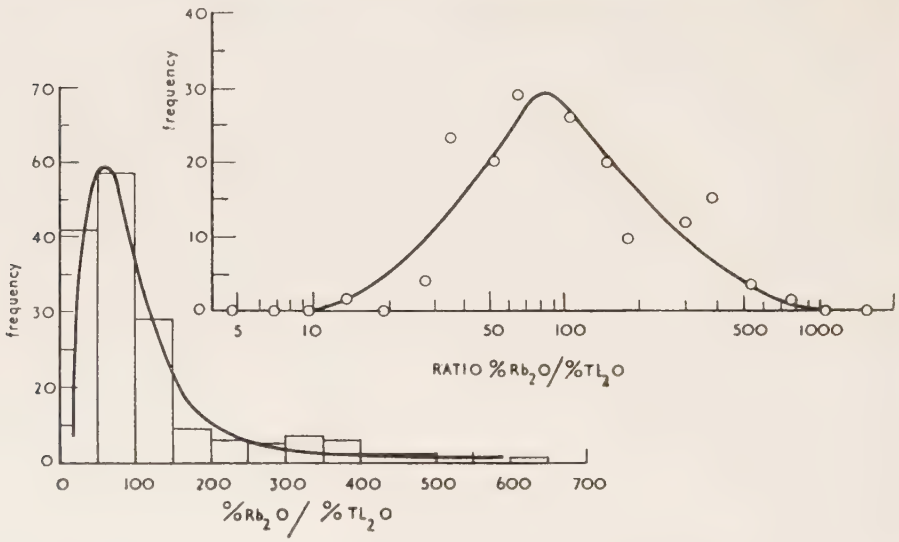

Fig. 5. Histograms for Rb_2O/Tl_2O and log (Rb_2O/Tl_2O) in potassium minerals.

calculate as 0·33 and 2·1, respectively; $\frac{am}{gm} = 1{\cdot}36$. Positive skewness is eliminated when $\log \frac{Rb_2O}{Tl_2O}$ is made the variate (after Ahrens, 1948). In place of using transformed data, a log scale has been used as abscissa, with 1·4 as the power factor to give the interval.

The log plot in Fig. 5 illustrates the difficulties which are inevitably introduced by geographical weighting and the inability to define precisely what should be considered a specific geological substance. The conspicuously high frequency of the ratio at ~400 is due to the fact that the Loolekop-Palabora pegmatites of the eastern Transvaal (see Ahrens, 1948) were represented by a fairly large number of specimens each with a characteristically high Rb/Tl ratio, whereas the conspicuously high frequency at ~40 is due mainly to muscovite; the ratio is quite often lower in this mineral than in other potassium minerals, and muscovite should therefore perhaps be omitted. The distribution of $\log \frac{Rb_2O}{Tl_2O}$ does, however, quite clearly approach lognormality despite these irregularities.

Rb in biotite and Li in muscovite

The histogram in Fig. 6 is for Rb_2O in thirty-six specimens of biotite from igneous rocks, mainly granite from North America (Whiting, 1951). The distribution shows decided positive skewness, and may be compared with that of log Rb_2O (Fig. 3), where the curve constructed on the basis of assumed lognormality fits

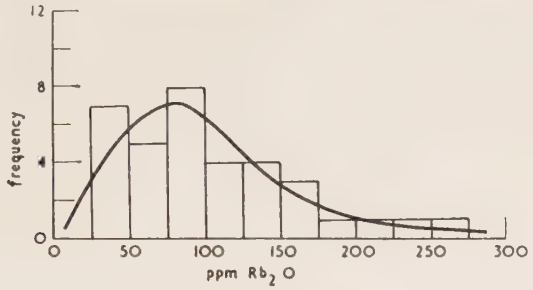

Fig. 6. Histogram for Rb_2O in biotite from igneous rocks.

the observed data very well (see above in this respect). Dispersion is moderate, and C, λ, and λ' calculate at 54 per cent, 0·235, and 0·17, respectively; $\frac{\text{am}}{\text{gm}} = 1{\cdot}16$. Extreme dispersion is shown by Li in forty-two specimens of muscovite, mainly

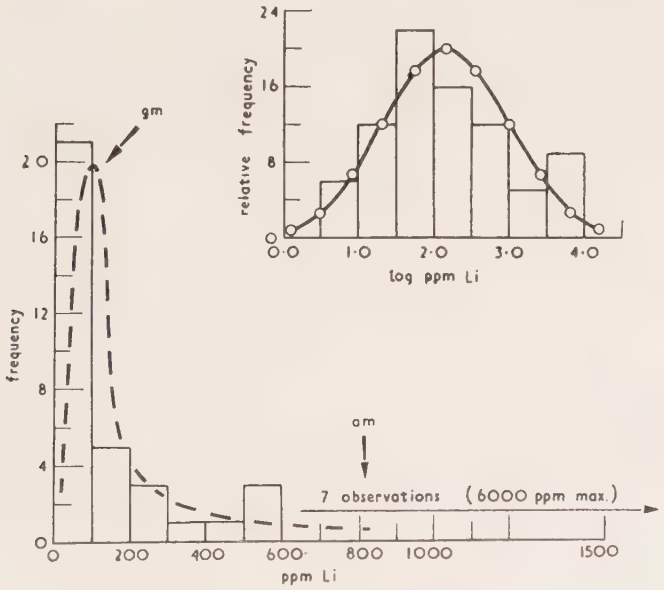

Fig. 7. Histogram for Li in muscovite. An example of extreme positive skewness. Note location of arithmetic mean (am).

from pegmatites (Ahrens and Liebenberg, 1945) and C, λ, and λ' calculate at 150–200 per cent, 0·83, and 6·7, respectively; $\frac{\text{am}}{\text{gm}} = 5.9$. The untransformed data show extreme positive skewness (Fig. 7), whereas that of log Li is fairly well

fitted by the curve which has been constructed on the basis of assumed log-normality, using the observed parameters and an interval of $\frac{1}{2}\ \lambda$.

Sr/Ca in limestone

The ratio of Sr to Ca in 165 specimens of limestone has been examined by Kulp, Turekian, and Boyd (1952), and using Sr/1000 Ca as variate, they obtained a histogram which shows decided positive skewness. Skewness is almost eliminated by using log Sr/1000 Ca as variate, and the array is fairly symmetrical and bell-shaped (Fig. 8); λ and λ' calculate as 0·36 and 2·3; $\frac{\text{am}}{\text{gm}} = 1{\cdot}42$.

For examples of distributions closely approaching lognormality in sediments, see Krige (1952; 1953), Sichel (1951—particularly the discussion at the end of

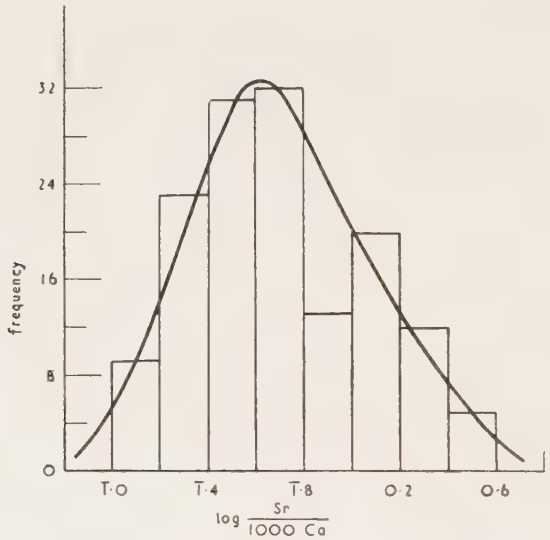

Fig. 8. Histogram for Sr/Ca ratios in limestone.

the paper), Ross (1951), and Koczy (1950). The papers of Krige, Sichel, and Ross are concerned particularly with the distribution of Au in conglomerate from mines of the Witwatersrand and the Orange Free State, South Africa, and are of considerable practical interest, as much exploration is now being carried out on the basis of assumed lognormality. See also Hancock (1948a and b) with respect to exploration on the basis of assumed lognormality.

The Significance of the Magnitude of Dispersion for Estimating the Abundances of Elements

Calculations of the abundances of elements in specific geological materials are based on averaging the analyses of several samples which have either been analyzed individually or in the form of a composite.* The accuracy with which such

* The reprehensible practice of using composites is stressed by Shaw and Bankier (1954). It should be recalled that whereas the composite values provide us with the arithmetic mean, no information is provided about the magnitude of dispersion, the type of distribution, or the magnitude of the most prevalent concentration.

abundances are estimated depends on the number of samples which have been analyzed and on the magnitude of dispersion of concentration of the elements in question. The accuracy of the method of analysis is another factor, often unknown, but for the present purpose of briefly examining the significance of the magnitude of dispersion, this will be ignored.

Consider Ga, Zr, and Cr in Canadian granite (AHRENS, 1954). As distribution of concentration may be considered lognormal, it will be more convenient to deal with the arithmetic mean of the log values (the antilog of which, the geometric mean, is an estimate of the most frequent concentration) rather than the arithmetic mean (the abundance of the element) of the untransformed data. Dispersion of Ga is very small ($\lambda = 0{\cdot}07$), that of Zr is moderate ($\lambda = 0{\cdot}18$), whereas

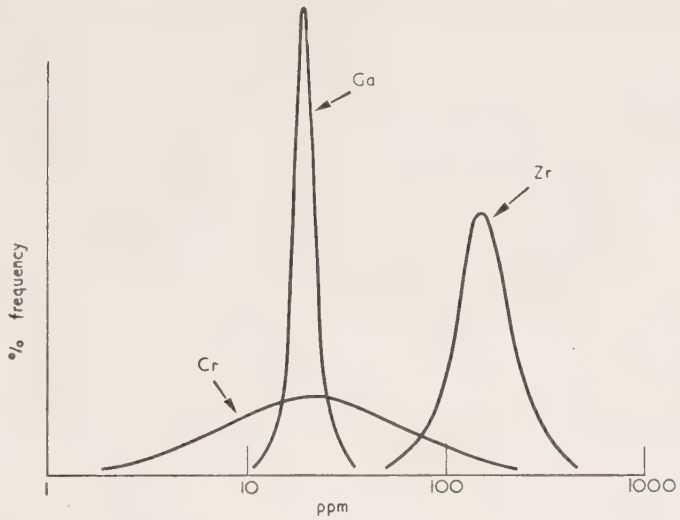

Fig. 9. Distribution curves for Ga ($\lambda = 0{\cdot}07$), Zr ($\lambda = 0{\cdot}18$), and Cr ($\lambda = 0{\cdot}54$) in Canadian granite.

that of Cr is extreme ($\lambda = 0{\cdot}54$). (Distribution curves—from Fig. 21 of AHRENS, 1954—for Ga, Zr, and Cr are given in Fig. 9 and illustrate the variation of magnitude of dispersion). Hence, whereas accurate estimates of the abundance of Ga in granite may be made on the basis of the analyses of a very few samples, a far larger number of specimens must be analyzed in order to estimate the abundance of Cr with equal accuracy. The following comparison will illustrate this quantitatively. We wish to estimate the most prevalent concentration of each of these three elements to within, say, half of the standard deviation for Ga ($\frac{1}{2}\lambda$ for Ga $= 0{\cdot}035$); that is, to within $\sim \pm 6\%$. As dispersion varies as $\frac{\lambda}{\sqrt{n}}$ $\left(\text{and not } \frac{\lambda}{n}\right)$, ($n$ = number of observations), Ga should be determined in four specimens to reduce the magnitude of λ to $\frac{1}{2}\lambda$. For Zr, twenty-six specimens should be analyzed, whereas for Cr the number is as large as 240. (The ratio of specimens required for estimates of equal accuracy is, thus, Ga : Zr : Cr : : 1 : 7 : 60.) It is not implied that such a rigid scheme should ever be adopted for abundance calculations—the accuracy with which dispersion is known is, in any case, probably not much

better than semi-quantitative—but these numbers emphasize quite definitely that much more attention should be given to the magnitude of the dispersion of concentration when attempting to estimate abundances; this factor is usually ignored.

The Arithmetic Mean (Abundance) and the Geometric Mean (an Estimate of the Most Frequent Concentration)

An examination of the relationship between the ratio of the arithmetic mean (abundance of an element) to the geometric mean (an estimate* of its most prevalent concentration) and the magnitude of dispersion (as expressed by λ or λ')

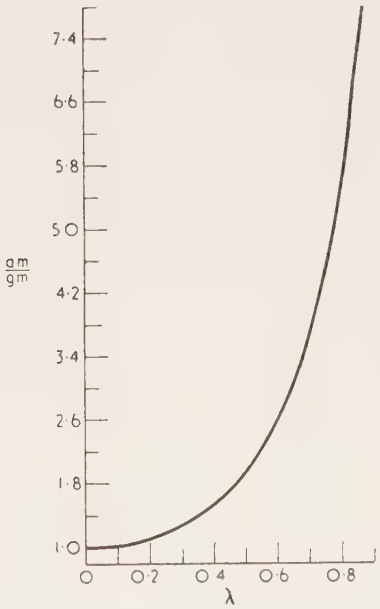

Fig. 10. The relationship between $\frac{am}{gm}$ and λ for a lognormal distribution.

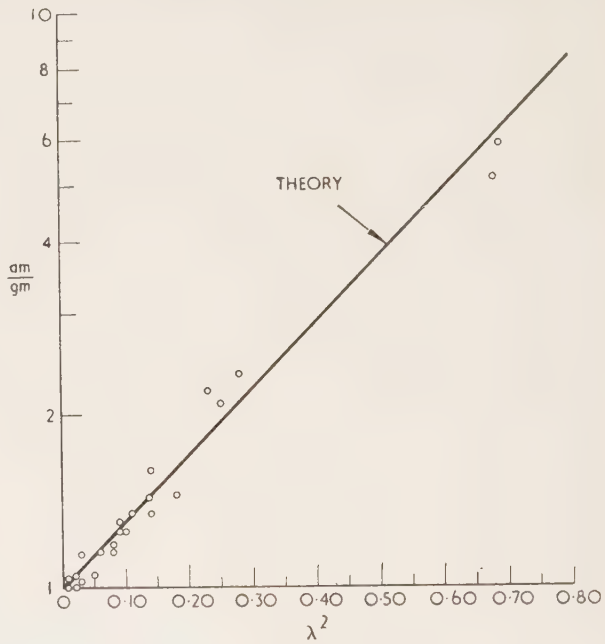

Fig. 11. The observed regularity between $\frac{am}{gm}$ and λ^2 is well developed and follows the curve calculated on the basis of assumed lognormality quite closely.

for all sets of observations revealed a regularity (Ahrens, 1954, Fig. 23) which was regarded as fairly quantitative. Finney (1954) (see also Badger, 1948), has since pointed out that the expression

$$\log am = \log gm + 1{\cdot}1513\,\lambda^2 \quad . \tag{1}$$

or

$$\log \frac{am}{gm} = 1{\cdot}1513\,\lambda^2 \tag{2}$$

holds for a lognormal distribution. Fig. 10 relates $\frac{am}{gm}$ to λ, as calculated from

* It should be recalled that calculated geometric means have thus far accorded closely with observed modes of the distribution curves (Ahrens, 1954, and this paper).

Eq. (1) or Eq. (2), and may be compared with Fig. 23 of AHRENS (1954). Accordance is close, except at extremely high dispersion. This relationship between theory and observation may be examined more critically by inspection of Fig. 11, a plot of $\log \frac{am}{gm}$ vs. λ^2. The plotted points refer to all observations examined thus far (AHRENS, 1954, and this paper), whereas the straight line is from Eq. (2). The fit of observed points about this line is generally satisfactory, and may be regarded as providing further general support of the lognormality of the distribution of the elements as a whole. If lognormality is assumed, Eq. (2) (or Fig. 11) may be regarded as an exact statement of the subsidiary geochemical law (AHRENS, 1954; see corollary referred to by CHAYES, 1954), which may be written as

$$\log \frac{\text{abundance}}{\text{most frequent concentration}} = 1{\cdot}15\ \lambda^2.$$

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GEOCHEMICAL RESEARCH

List of persons doing research of interest to geochemists and their current work

prepared by

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Michael Fleischer (U.S. Geol. Survey, Washington, D.C.)*

The Commission on Geochemistry (formerly called the Commission on Geochemical Localization of the Elements) of the International Union of Pure and Applied Chemistry was organized in 1951. At its first meeting in New York in Sept., 1951, it was agreed that it was highly desirable to prepare a list of current research activity in geochemistry. Announcements were published in many journals in 1952 and these were supplemented by questionnaires sent to many individuals and research laboratories.

The present list summarizes the information received. Since many persons did not reply, we have given research projects based on published information for many. Those in quotation marks are from replies or direct communication; those not in quotation marks were inserted by us.

It is our hope that this list will aid researchers to get in touch with others working along similar lines. We believe that such communication is highly important and beneficial. We regret, therefore, that the list is so incomplete. In particular, no replies were received from Czechoslovakia, Hungary, Poland, or the U.S.S.R., so that many important centres of geochemical research are not represented in this list.

1. Abelson, P. H.; Geophysical Lab., 2801 Upton St., N.W. Washington, D.C.
2. Adler, Isadore and Axelrod, J. M.; U.S. Geol. Survey, Washington, 25, D.C.
   "X-ray flourescence analysis."
3. Ahrens, L. H.; Dept. Mineralogy, Oxford Univ., Oxford, England.
   "Ionic radii and ionization potentials; Geological age by the rubidium-strontium method; Minor elements in rocks." See Walker, F.
4. Aldershoff, W. G.; Univ. Leiden, Netherlands.
5. Aldrich, L. T., Davis, G. I. and Tilton, G. R.; Lab. of Terrestrial Magnetism, Carnegie Institution of Washington, Washington, D.C.
   "Isotopic analysis of Sr and Pb; Geological age by Rb-Sr, K-Ca, and K-A methods."
6. Allen, V. T., St. Louis Univ., St. Louis, Mo.
   Genesis of bauxite and clays.
7. Almond, Hy.; see Lakin, H. W.
8. Alpher, R. A.; Applied Physics Lab., Johns Hopkins Univ., Silver Spring, Md.
   Origin of elements.
9. Altschuler, Z. S.; U.S. Geol. Survey, Washington 25, D.C.
   "Uranium in phosphates."
10. Anderson, C. A.; U.S. Geol. Survey, Washington 25, D.C.
    Ore deposits.
11. Anderson, J. S.; Atomic Energy Research Establishment, Harwell, England.
    Minor elements in ore minerals.
12. Andreatta, Ciro and Emiliani, F.; Inst. Mineral., Petrog., Univ. Bologna, Italy.
    "Trace elements in pegmatites of the Eastern Central Alps."
13. Arrhenius, Gustaf; Scripps Inst. of Oceanography, La Jolla, Calif.
    Oceanic sediments.
14. Asari, Tamiya; Scientific Research Inst., Tokyo.
    Geochemistry of strontium.
15. Assarsson, Gunnar; Sver. Geol. Undersokning, Stockholm.
    Chemistry of natural brines.

* Publication authorized by the Director, U.S. Geological Survey.

16. Axelrod, J. M.; see Adler, I.
17. Bader, R. G.; Dept. Oceanography, Univ. Washington, Seattle, Wash.
"Organic chemistry of marine sediments."
18. Baertschi, Peter, Schwander, H., and Wenk, E.; Phys.-Chem. Anstalt, Univ. Basel, Switzerland.
"Abundances of O isotopes in silicate rocks; Abundances of O and C isotopes in carbonate rocks."
19. Bailey, E. H.; U.S. Geol. Survey, Menlo Park, Calif.
Chemistry of mercury deposits.
20. Bannister, F. A., Jaag, and Wiseman, J. D. H.; British Museum Natural History, London.
"Cores from the bottom of Lake Zürich."
21. Barth, T. F. W.; Mineralog. Museum, Univ. Oslo, Norway.
"Petrographic calculations of Norwegian rock analyses."
22. Bates, T. F.; Pennsylvania State Univ., State College, Penn.
"Mineralogy of uranium-bearing shales."
23. Beath, O. A.; Univ. Wyoming, Laramie, Wyo.
Selenium in plants, soils, and rocks.
24. Becker, E. W.; Univ. Marburg, Germany.
Abundance of C^{13} and O^{18}.
25. Beers, R. F.; Rensselaer Polytechnic Inst., Troy, N.Y.
"Geochemistry of black shales."
26. Behre, C. H., Jr.; Columbia Univ., New York 27, N.Y.
Ore deposits.
27. Bennett, W. H.; Colonial Geol. Surveys, London.
Analysis of rocks and ores.
28. van Bemmelen, R. W.; Univ. Utrecht, Netherland.
29. Benoit, R. J.; Yale Univ., New Haven, Conn. (with G. E. Hutchinson)
"The cobalt cycle in lakes."
30. Berbeyer, R. M.; Lab. Nacional de Fomento. Industrial, Lomas de Sotelo, Tecamachalco, Mexico D.F.
"Geochemistry of ground water, hot springs, and volcanoes."
31. Bertrand, Didier; Pasteur Inst., Paris.
Trace elements in plants.
32. Bianchi, Angelo; Inst. Mineral., Petrog., Univ. Padova, Italy.
"Petrochemistry of Alpine intrusives."
32b. Bienner, F.; Inst. Français du Pétrole, Rueil-Malmaison, Paris, France.
Geochemistry of petroleum.
33. Billings. M. F.; Harvard Univ., Cambridge 38, Mass.
34. Birch, Francis; Harvard Univ., Cambridge, Mass.
Geophysics; Temperatures within the Earth.
35. Björlykke, Harold; Norsk Bergverk, Oslo, Norway.
Minor elements in ore minerals.
36. Blumer, Max; Amsterdam.
Minor elements in sediments and bitumens.
37. Boato, G.; Inst. Nuclear Studies, Univ. Chicago, Chicago 37, Ill.
Isotopic constitution of H, C, and N in rocks and meteorites.
38. Borchert, Hermann, and Otte, V.; Bergakad., Clausthal, Germany.
"Spurenelemente in Steinkohlenaschen; Spurenelemente der Gangmineralien der Erzlagerstätten."
39. Bowen, N. L.; Geophysical Lab., 2801 Upton St., N.W., Washington, D.C.
Evolution of igneous rocks.
40. Bowie, S. H. U.; see Davidson, C. F.
41. Boyd, G. E.; Oak Ridge National Laboratory, Oak Ridge, Tenn.
"Possible natural occurrence of technetium."

42. Brannock, W. W. and Shapiro, Leonare; U.S. Geol. Survey, Washington 25, D.C.
"Rapid methods of rock analysis." See also D. E. White.
43. Breger, Irving and Deul, Maurice; U.S. Geol. Survey, Washington 25, D.C.
"Geochemistry of carbon; Association of uranium with carbonaceous materials."
44. Brewer, F. M.; Dept. Chemistry, Oxford Univ., Oxford, England.
"Spectrographic determination of trace elements in the zoned lead-zinc ores of the North Pennines; Distribution of germanium and gallium in sphalerite and other sulphides; General consideration of trace elements in sulphides."
45. Brown, H. S., Patterson, C. C., and Uchiyana, Aiji; Calif. Inst. Technology, Pasadena 4, Cal.
Abundances of elements in meteorites; Uranium in igneous rocks; Mass spectrograph studies.
46. Buddington, A. F.; Princeton Univ., Princeton, N.J.
Petrology of igneous and metamorphic rocks; Relation of magnetism of rocks to their content of Fe and Ti minerals.
47. Buljan, Miljenko; Inst. Oceanography, Split, Jugoslavia.
"Chemistry of sea water; Effect of phosphate; Ratio SO4:CI; Oxidation of H_2S; Variation of salinity in the Adriatic Sea; Cyclic salts; Abundance of elements in organisms; Effect of volcanic material introduced into the sea."
48. Burbank, W. S.; U.S. Geol. Survey, Washington 25, D.C.
Thermodynamics of ore formation; Alteration associated with ore deposits.
49. Burri, Conrad; Eidgen. Tech. Hochschule, Zürich, Switzerland.
Petrology of igneous and metamorphic rocks.
50. Butler, J. R.; Rothamsted Exptl. Sta., Harpenden, England.
Geochemistry of rock weathering.
51. Callaghan, Eugene; New Mexico Bureau of Mines, Socorro, N. Mex.
Petrology of rhyolitic rocks; Perlite.
52. Cameron, E. N.; Univ. Wisconsin, Madison, Wis.
Ore deposits; Optical and chemical study of ore minerals.
53. Canney, F. C.; U.S. Geol. Survey, Denver 14, Colo.
Geochemical prospecting. See Myers, A. T.
54. Cannon, Helen; U.S. Geol. Survey, Washington 25, D.C.
Biochemical prospecting.
55. Cannon, R. S.; U.S. Geol. Survey, Washington 25, D.C.
Mass spectrograph studies of the isotopic constitution of the ore metals.
56. Carobbi, Guido; Inst. Mineral., Petrog., Geochim., Univ. Firenze, Italy.
"Geochemistry of boron and fluorine; Diffusion of boron in the rocks of Elba."
57. Carpanese, Tullio; Univ. Padova, Italy.
58. Chapman, R. W.; see Larsen, E. S., Jr.
59. Carron, M. K.; see Murata, K. J.
60. Chalmers, R. A.; Dept. Geol., Univ. Durham, England.
"New methods of microchemical analysis applied to rocks and minerals."
61. Charles, G.; Lab. Geol. Agric. Ecole Natl. Agric., Algiers.
"Le cycle géochimique du phosphore; Le phosphore dans les roches sédimentaires, les eauxs, et les sédiments actuels."
62. Chayes, Felix; Geophysical Lab., 2801 Upton St., N.W., Washington, D.C.
Composition and petrography of granitic rocks.
63. Chodos, A. A.; Calif. Inst. Technol., Pasadena 4, California.
Spectrographic determination of minor elements in rocks and minerals.
64. Choubert, Boris; Inst. franc. d' Amerique Tropicale, 104 Rue Caulaincourt, Paris.
Geochemistry of magmatic rocks.
64b. Clews, C. J. B.; Dept. Physics, Univ. W. Australia, Nedlands.
"C_{12}/C_{13}-ratio in rocks; U/Pb and Sr/Rb for age determinations."
65. Coats, R. R.; U.S. Geol. Survey, Washington 25, D.C.
Minor elements in igneous rocks; Geochemistry of sulphur.

66. Coleman, L. C.; see Hess, H. H.
67. Collins, C. B.; Univ. Toronto, Ontario.
Geological age by lead-uranium method.
68. Contaut, H.; Lab. d' Analyse, Saint-Max-Les Nancy, France.
"Sur le comportement de certains sediments en profondeur."
69. Conway, E. J.; Dept. Biochem. and Pharmacology, Univ. Dublin, Ireland.
"Geochemistry of the alkali metals".
70. Cornwall, H. R.; U.S. Geol. Survey, Houghton, Mich.
Association of copper with igneous rocks.
71. Correns, C. W.; Inst. Sediment. Petrog., Univ. Gottingen, Germany.
"Geochemie des Zinks, des Chlors und Broms, des Bleis";
"Geochemie der Diagenese (Fe, Mn, Ti)."
72. Cotelo Neiva, J. M.; Univ. Coimbra, Portugal.
Geochemistry of waters; Association of nickel and platinum with ultramafic rocks.
73. Craig, Harmon; Inst. Nuclear Studies, Univ. Chicago, Chicago 37, Ill.
Carbon isotopes; Composition of meteorites.
74. Daniels, Farrington and Saunders, D. F.;
Univ. Wisconsin, Madison, Wis.
Uranium in volcanic rocks; Thermoluminescence.
75. Davidson, C. F. and Bowie, S. H. U.; Geol. Survey and Museum, London.
"Geochemistry of uranium and thorium."
76. Davis, G. L.; Geophysical Lab., 2801 Upton St., N.W., Washington, D.C.
See Aldrich, L. T.
77. Deer, W. A.; Univ. Manchester, England.
"Geochemistry of the Lewisian and Moinean pegmatites; Geochemical investigation of the manganese beds of the Harlech Dome, Wales."
78. Deevey, E. S., Jr. and Livingstone, Daniel; Geochronometric Lab., Yale Univ., New Haven, Conn.
"Application of radiocarbon dating to limnological studies."
79. Deicha, G; St. Germain-en-Laye, France.
Temperature of formation of minerals from study of liquid inclusions.
80. Dennen, W. H.; Mass. Inst. Technology, Cambridge 39, Mass.
"Minor elements in rocks."
81. Deul, Maurice; see Breger, Irving.
82. DeVore, George; Univ. Chicago, Chicago 37, Ill.
Migration of elements in metasomatic processes.
83. Dunham, K. C. and Phillips, R.; Univ. Durham, England.
"Geochemistry of the magnesian limestone of Durham."
84. Dutta, R. K. and Mukherjee, B.; Univ. College, Calcutta, India.
Germanium in sphalerite; minor elements in coal ash.
85. Dutton, Carl; U.S. Geol. Survey, Madison, Wis.
Iron ores.
86. von Eckermann, Harry; Edeby, Sparreholm, Sweden.
Barium and strontium in alkalic rocks.
87. Edwards, A. B.; Univ. Melbourne, Australia.
Petrology of igneous rocks; Origin and textures of ore minerals.
88. Efremov, N.; 1061 Intervale Ave., New York, 59, N.Y.
Origin of elements; Ultramafic rocks.
89. Eitel, Wilhelm; Toledo Univ., Toledo, Ohio.
Silicate chemistry.
90. Ellestad, R. B.; Metalloys Corp., Minneapolis, Minn.
Lithium.
91. Emiliani, F.; see Andreatta, C.
92. Engel, A. E. J.; Calif. Inst. Technology, Pasadena 4, Cal.
Geochemistry of metamorphic processes.

93. Engelhardt, Wolf von; Kollenrodstr. 4, Hannover, Germany.
94. Epstein, Samuel; Calif. Inst. Technol., Pasadena 4, Cal.
Isotopic studies on carbonates.
95. Erd, R. C.; see Faust, G. T.
96. Erickson, R. L.; U.S. Geol. Survey, Denver 14, Colo.
Alkalic rocks of Magnet Cove, Ark.
97. Eskola, Pentti; Univ. Helsinki, Finland.
98. Evrard, Pierre; 54 Rue de Taciturne, Bruxelles, Belgium.
Minor elements in ore minerals; Geochemistry of iron and titanium.
99. Fahey, J. J.; U.S. Geol. Survey, Washington 25, D.C.
"Geochemistry of salines of the Green River formation, Wyoming."
100. Fairbairn, H. W.; Mass. Inst. Technology, Cambridge 39, Mass.
Minor elements in rocks; Accuracy of chemical analyses.
101. Fairbridge, R. W.; Univ. W. Australia, Nedlands.
"Limestone erosion in the inter-tidal belt; $CaCO_3$ solubility and cycle."
102. Faust, G. I.; U.S. Geol. Survey, Washington 25, D.C.
"Differential thermal analysis of carbonates and hydrous silicates; The hydrous magnesium silicates; (and Erd, R. C.) Petrology of the Watchung basalts."
103. Feiss, J. W.; Kennecott Copper Corp., 161 E. 42nd St., New York 17, N.Y.
Geochemical associations of ore metals.
104. Fenoglio, Massimo; Inst. Mineral., Petrog. Univ. Torino, Italy.
Nickel in ultramafic rocks.
104b. Festa, C.; Inst. Geofisica, Rome, Italy.
Radioactivity.
105. Fester, G. A.; Univ. nacl. litoral. Santa Fe, Argentina.
106. Fischer, R. P.; U.S. Geol. Survey, Grand Junction, Colorado.
Ore deposits of uranium and vanadium.
107. Fleischer, Michael; U.S. Geol. Survey, Washington 25, D.C.
"Revision of Clarke's Data of Geochemistry; Geochemistry of ore minerals; Minor elements in manganese oxides."
108. Fletcher, M. H.; see Grimaldi, F. S.
109. Foote, P. D.; Gulf Research and Development Co., Pittsburgh 30, Pa.
Geochemistry of sedimentary rocks; Rock alteration.
110. Földvari, Aladar; Geol. Survey Hungary, Budapest.
Uranium in igneous rocks.
111. Földvari, Maria; Geol. Survey Hungary, Budapest.
Minor elements in volcanic rocks.
112. Fornaseri, Mario; Univ. Rome.
113. Foshag, W. F.; U.S. Natl. Museum, Washington, D.C.
"Chemistry of lavas, fumaroles, and sublimates of Paricutin Volcano."
114. Foster, M. D.; U.S. Geol. Survey, Washington 25, D.C.
"Geochemistry of clays."
115. Franco, R. R.; Univ. São Paulo, Brazil.
116. Frederickson, A. F.; Washington Univ., St. Louis, Mo.
Weathering of rocks.
117. Friedman, Irving; U.S. Geol. Survey, Washington 25, D.C.
Hydrothermal synthesis; Mass spectrographic studies. See Graf, D. L.
118. Frondel, Clifford and Frondel, J. W.; Harvard Univ., Cambridge 38, Mass.
"Mineralogy of uranium."
119. Gabrielson, Olof; Sver. Geol. Undersökn., Stockholm, Sweden.
120. Gallitelli, Paolo; Univ. Modena, Italy.
121. Garrels, R. M.; U.S. Geol. Survey, Washington 25, D.C.
"Fate of uranium in weathering; Oxidation-reduction potentials; Stability of minerals in aqueous solution at low temperatures and pressures."

122. Gault, H. R.; Lehigh Univ., Bethlehem, Pa.
Geochemistry of carbonate rocks.
123. Gavelin, Sven; Mineral. Inst., Univ. Stockholm.
"C isotopes in pre-Cambrian rocks." See Wickman, F.
124. Gibson, D. T.; Univ. Glasgow, Scotland.
125. Godwin, H.; Univ. Cambridge, England.
Age by C^{14} method.
126. Goldberg, E. D.; Scripps Inst. of Oceanography, La Jolla, Cal.
"Compilation of analyses of sea water; Abundances of elements in sea waters."
127. Goldich, S. S.; Rock Analysis Lab., Univ. Minnesota, Minneapolis 14, Minn.
"Methods of rock analysis; Geochemistry of Duluth gabbro."
128. Goldsmith, J. R.; Univ. Chicago, Chicago 37, Ill.
Hydrothermal synthesis of silicates; Crystal chemistry. See Graf, D. R.
129. Gottfried, David; see Larsen, E. S., Jr.
130. Graf, D. L.; Illinois Geol. Survey, Urbana, Ill.
The synthesis of rhombohedral carbonates and determination of their stability fields (with Friedman, I. and Goldsmith, J. R.).
131. Graham, R. P.; McMaster Univ., Hamilton, Ontario.
"Relative abundances of chlorine isotopes in minerals."
132. Graton, L. C.; Harvard Univ., Cambridge 38, Mass.
Origin of ore-forming fluids.
133. Green, Jack; California Co., P.O. Box 1277, Bismarck, North Dakota.
Geochemical table of the elements.
134. Greig, J. W.; Geophysical Lab., 2801 Upton St., N.W., Washington, D.C.
134b. Grigg, F. J. T.; Director of Dominion Laboratory, Wellington (1), New Zealand.
135. Grim, R. E.; Univ. Illinois, Urbana, Ill.
Clays and clay minerals.
136. Grimaldi, F. S., Fletcher. M. H., Kinser, C. A., May, I. H., and Rader, L. S.; U.S. Geol. Survey, Washington 25, D.C.
"Analytical chemistry of uranium and thorium."
137. Grip, Erland; Boliden Mining Co., Boliden, Sweden.
Minor elements in sulphide ores.
138. Groves, A. W.; Colonial Geol. Surveys, London.
139. Gruner, J. W.; Univ. Minnesota, Minneapolis, Minn.
Hydrothermal synthesis; Conditions of formation and stability of uranium minerals.
140. Guimaraes, Djalma; Inst. Technol. Industrial, Belo Horizonte, Brazil.
Geochemistry of granitization; Zirconium and uranium in alkalic rocks.
141. Gulbrandsen, R. A.; U.S. Geol. Survey, Spokane, Wash.
See McKelvey, V. F.
142. Haberlandt, Herbert; Mineral. Inst., Univ. Vienna.
"Elementvergesellschaftung und Elementwanderungen im Gebiete der radioaktiven Heilquellen und Goldlagerstätten von Bad-Gestein; Elementvergesellschaftung und Mikroparagenese seltener Elemente, vor allem in alpinen Zinkblenden und Bleiglanzen; Spurenelementbestimmungen in Feldspaten alpiner Gesteinen; Fluoreszenzanalyse seltener Erden in verschiedenen Mineralien."
143. Hammer, A. J.; Bowling Green State Univ., Bowling Green, Ohio.
"Geochemistry of vanadium; Preparation of a comprehensive bibliography on clays."
144. Harris, P. G.; Dominion Lab., Wellington, New Zealand.
"Composition of glassy volcanic rocks; Weathering products of basalt; Paragenetic mineralogy of New Zealand ultrabasic rocks."
145. Harvey, C. O.; Geol. Survey Great Britain, London.
Chemical and spectrographic methods of analysis of rocks.
146. Harvey, H. W.; Marine Lab., Plymouth, England.
Chemistry of the sea.
147. Hastings, W. W.; see Love, S. K.

148. Hatch, R. A.; U.S. Bureau of Mines, Norris, Tenn.
"Synthesis of fluor-micas and fluor-amphiboles."
149. Hawkes, H. E.; Mass. Inst. Technol., Cambridge 39, Mass.
Geochemical prospecting for ore deposits.
150. Hawley, J. E.; Queen's Univ., Kingston, Ontario.
"Platinum metals in ore minerals; Minor elements in granitic rocks; Trace elements in Nova Scotia coals."
151. Headlee, A. J. W.; West Virginia Geol. Survey, Morgantown, W. Va.
"Minor elements in coal; Minor elements in sedimentary rocks."
152. Hecht, Friedrich; Chem. Inst., Univ. Vienna.
"Mikroanalytische Bestimmungen, insbesondere Uran und Thorium."
153. Hedgpeth, J. W.; Scripps Inst. Oceanography, La Jolla, Cal.
Chemistry of lakes and closed basins.
154. Heé, Arlette; Inst. Phys. du Globe, Strasbourg, France.
"Localisation des matières radioactives dans les roches."
155. Hegemann, Friedrich; Mineral.-Geol. Inst., Tech. Hochschule, Munchen, Germany.
Minor elements in ore minerals.
156. Heide, F.; Mineral. Inst., Univ. Jena, Germany.
"Geochemie der Süsswässer; Konzentration der Saale an F, Cl, Br, I, Cu, Zn, Ag, Au, Pt, Li, Na, K, Rb, Cs, Be, Mg, Ca, Sr, Ba, Fe, Co, Ni; Vergleichende Geochemie der variskischen und pravariskischen Granite; Untersuchung der Phosphid—und Carbidschmelze der Meteoreisen."
157. Heinrich, E. W.; Mineral. Lab., Univ. Michigan, Ann Arbor, Mich.
Composition and paragenesis of pegmatite minerals.
158. Helz, A. W. and Waring, C. L.; U.S. Geol. Survey, Washington 25, D.C.
"Spectrographic methods of analysis of rocks and minerals."
159. Hem, J. D.; U.S. Geol. Survey, Albuquerque, N. Mex.
Geochemistry of ground waters.
160. Henderson, E. P.; U.S. Natl. Museum, Washington 25, D.C.
"Composition of meteorites."
161. Hess, H. H.; Dept. Geol., Princeton University, Princeton, N.J.
(With L. C. Coleman) "Variation of optics and unit cell with composition in the clinopyroxenes"; (with J. R. Smith) "Variation of optics with composition of intermediate plagioclases."
162. Hey, M. H.; British Museum Natural History, London.
"Rock and mineral analyses."
163. Hietanen, Anna; U.S. Geol. Survey, Menlo Park, Cal.
Petrology of metamorphic rocks: Metasomatic processes.
164. Higazy, R. A.; Geol. Dept., Univ. Alexandria, Egypt.
"Trace elements in rocks."
165. Hoehne, Karl; Völklingen, Saar.
Arsenic and antimony in ore minerals.
166. Holland, H. D.; Dept. Geol., Princeton Univ., Princeton, N.J.
"Effect of radiation on the structure and physical properties of zircon."
167. Holmes, Arthur; Grant Inst. Geol., Univ. Edinburgh, Scotland.
"Dating the pre-Cambrian rocks of Africa and India by investigations of radioactive minerals."
168. Holser, W. T.; Cornell Univ., Ithaca, N.Y.
Geochemistry of beryllium.
169. Hooker, Marjorie; U.S. Geol. Survey, Washington 25, D.C.
"Revision of Washington's compilation of analyses of igneous rocks."
170. Houtermans, F. G.; Univ. Berne, Switzerland.
Geological age by lead-uranium method.
171. Howie, R. A.; Dept. Mineral Petrog., Cambridge Univ., England.
"Geochemistry of the charnockite rock group."

172. Hügi, Th; Dept. Mineral., Univ. Berne, Switzerland.
Spectrographic methods applied to problems of petrology.
173. Hurley, P. M.; Mass. Inst. Technol., Cambridge 39, Mass.
"Uranium, thorium, and potassium in rocks, especially basalts, for the determination of age and production of heat; Isotope ratios of Ca, K, and A in rocks and minerals; Radio-element equilibrium studies in ocean bottom cores."
174. Hutchinson, G. E.; Osborn Zoological Lab., Yale Univ., New Haven, Conn.
Biogeochemistry of iodine and bromine (with E. M. Low); Translation of Vinogradov's Chemical Composition of Marine Organisms; Atmospheric gases; Limnology." See R. J. Benoit, J. R. Vallentyne.
175. Huttenlocher, H.; Univ. Berne, Switzerland.
176. Hutton, C. O.; Stanford University, Palo Alto, Cal.
Residual deposits.
177. Ingerson, Earl, and Richter, D. H.; U.S. Geol. Survey, Washington 25, D.C.
"Temperatures of formation of minerals from study of inclusions; Hydrothermal syntheses."
178. Ishibashi, Masayoski; Dept. Analytical Chemistry, Univ. Kyoto, Japan.
"Oceanic salts and sediments."
179. Ishimori, Tomitaro; Kyushu Univ., Fukuoka, Japan.
Molybdenum and chromium in volcanic rocks.
180. Iwasaki, Iwaji; Kyushu Univ., Fukuoka, Japan.
Geochemistry of hot springs; Geochemistry of volcanic rocks.
181. Jaag, ; see Bannister, F. A.
182. Jackson, M. L.; Dept. Soils, Univ. Wisconsin, Madison 6, Wis.
"Weathering of minerals in soils."
183. Jacob, K. D.; U.S. Dept. Agriculture, Beltsville, Md.
Chemistry of phosphate rock.
184. Jaffe, H. W.; see Larsen, E. S., Jr.
185. Jahns, R. H.; Calif. Inst. Technol., Pasadena 4, Cal.
Mineralogy and origin of pegmatites; Rare elements in pegmatites.
186. Jamieson, J. C.; Inst. Nuclear Studies, Univ. Chicago, Chicago 37, Ill.
Calcite-aragonite equilibrium.
187. Jasmund, Karl; Univ. Göttingen, Germany.
Solubility of salts at supercritical temperatures.
188. Jedwab, J.; Univ. Bruxelles, Belgium.
Spectrographic analysis of minerals.
189. Jensen, M. L.; Yale Univ., New Haven, Conn.
Diffusion in geological processes.
190. Joensuu, Oiva; Univ. Chicago, Chicago 37, Ill.
Spectrographic analysis of rocks and meteorites. See Rankama, K.
191. Jongejan, A.; 273 Wellington Heights, Sudbury, Ontario.
"Biogeochemical prospecting for nickel and copper."
192. Kaiser, E. P.; U.S. Geol. Survey, Denver 14, Colo.
"Geochemistry of niobium; Trace elements in mill and smelter products."
193. Kakihana, Hidetake, Nagoya Univ., Japan.
Minor elements in metallurgical wastes.
194. Keevil, N. B.; Mining Geophysics Corp., Toronto, Ontario.
Radioactivity and geological age.
195. Keith, M. L.; Pennsylvania State Univ., State College, Pa.
"Equilibrium in silicate systems." See Tuttle, O. F.
196. Keller, W. D.; Univ. Missouri, Columbia, Mo.
"Trace elements in limestones; Infra-red absorption spectra of minerals."
197. Kennedy, G. C.; Univ. California, Los Angeles 24, Cal.
P-V-T relations of water and carbon dioxide; Solubility in silicate-water systems.

198. Kennedy, W. Q.; Univ. Leeds, England.
Magmatic differentiation.
199. Kent, L. E.; Geol. Survey, P.O. Box 401, Pretoria, Union S. Africa.
Geochemistry of thermal waters.
200. Kerr, P. F.; Columbia Univ., New York 27, N.Y.
"Origin of uranium deposits at Marysvale, Utah; Alteration associated with ore deposits."
201. Kimura, Kenjiro; Dept. Chemistry, Univ. Tokyo.
"Geochemical prospecting for metallic ore deposits; Geochemical studies on hot springs in Japan; Distribution of radioactive elements in minerals of Japan; Distribution and resources of germanium."
202. Kinser, C. A.; see Grimaldi, F. S.
203. Knopf, Adolph; Stanford Univ., Palo Alto, Cal.
Geologic age; Igneous petrology.
204. Koczy, F. F.; Oceanograf. Inst., Goteborg, Sweden.
Oceanic sediments; Thorium in sea water.
205. Kohman, T. P. and Saito, Nobufusa; Carnegie Inst. Technol., Pittsburgh, Penn.
"Geological age by Pb^{210} method."
206. Koritnig, S.; Univ. Göttingen, Germany.
Geochemistry of fluorine.
206b. Kostov, I.; Mineralog. Inst., Sofia, Bulgaria.
"Age of radioactive minerals."
207. Kracek, F. C.; Geophysical Lab., 2801 Upton St., N.W. Washington, D.C.
Thermochemistry of minerals.
208. Krauskopf, K. B.; Stanford Univ., Palo Alto, Cal.
Thermodynamics of ore-forming processes.
209. Krejci-Graf, Karl; Geol. Inst., Univ. Frankfurt-au-Main, Germany.
"Characterization of sediments by their content in elements, isotopes, compounds, and crystal habit; Geochemistry of petroleum."
210. Krishnan, M. S.; Geol. Survey India, Calcutta.
"Analyses of rocks and minerals."
211. Krynine, P. D.; Pennsylvania State Univ., State College, Pa.
Sedimentary rocks.
212. Kubach, Isa; Gmelin Inst., Clausthal-Zellerfeld, Germany.
Geochemistry of silicon. See Pietsch, E.
213. Kuenen, P. H.; Geol. Inst., Univ. Groningen, Netherlands.
Geochemistry of sediments.
214. Kuiper, G. P.; Dept. Astronomy, Univ. Chicago, Chicago 37, Ill.
Terrestrial and planetary atmospheres.
215. Kulp, J. L.; Lamont Geol. Observatory, Columbia Univ., New York 27, N.Y.
"Natural radiocarbon measurements; Natural tritium measurements; Ionium method; Origin of native S in Gulf Coast salt domes; Strontium isotope ratios in limestone; Uranium-lead method of age determination; Natural helium measurements; K-A method of age determination."
216. Kuno, Hisashi; Univ. of Tokyo, Japan.
"Chemical analyses of volcanic rocks, including both major components and trace elements."
217. Kuroda, P. K.; University Arkansas, Fayetteville, Ark.
"Radioactivity of hot springs, rivers, and lake waters."
218. Kutina, Jan; Charles Univ., Prague, Czechoslovakia.
Minor elements in ore minerals.
219. Kvalheim, Aslak; Statens Rastoff Lab., Trondheim, Norway.
Spectrochemical analysis of ores.
220. Lakin, H. W., Almond, Hy., and Ward, F. N.; U.S. Geol. Survey, Denver 14, Colo.
Development of chemical methods for geochemical prospecting.

221. Lamar, J. E., Shrode, R. S. and Thomson, K. B.; Illinois Geol. Survey, Urbana, Ill.
"Trace elements in Illinois limestones and dolomites; Water-soluble salts in Illinois limestones and dolomites."
222. Lamar, W. L.; U.S. Geol. Survey, Columbus, Ohio.
Methods of analysis of waters.
223. Landergren, Sture; Sveriges Geol. Undersökn, Stockholm, Sweden.
"Carbon isotopes in marine sediments; Distribution of O isotopes in minerals; Geochemistry of deep-sea sediments; New methods of spectrochemical analyses of rocks; Distribution of the ferride elements in basalts." See Wickman, F.
224. Larsen, E. S., Jr., Chapman, R. W., Gottfried, David, Waring, C. L., and Jaffe, H. W.; U.S. Geol. Survey, Washington 25, D.C.
"Distribution of uranium in igneous rocks; Zircon method of determination of age of igneous rocks."
225. Larsen, E. S.; 3rd U.S. Geol. Survey, Washington 25, D.C.
"Mineralogy of opaque uranium and vanadium minerals."
226. Leininger, R. K.; Indiana Geol. Survey, Bloomington, Ind.
"Spectrographic determination of major and minor elements in limestones, coal ash, shales, and clays."
227. Leutwein, Friedrich; Mineralog. Inst., Bergakademie, Freiberg, Saxony, Germany.
"Geochemische Untersuchungen an Kohlenaschen; Geochemische Untersuchungen an Erzlagerstätten der Nichteisenmetalle."
228. Libby, W. F.; Univ. Chicago, Chicago 37, Ill.
Radiocarbon dating.
229. Liebenberg, W. R.; Geol. Survey, P.O. Box 401, Pretoria, Union S. Africa.
230. Lietz, Joachim; Univ. Hamburg, Germany.
Sulphides in salt dome rocks.
231. Lindberg, M. L.; U.S. Geol. Survey, Washington 25, D.C.
"Phosphate minerals of pegmatites."
232. Livingstone, Daniel; see Deevey, E. S.
233. Ljunggren, Pontus; Chelmers Tek. Hogskola, Gothenburg, Sweden.
Biogeochemistry of manganese.
235. Lopez de Azcona, J. M.; Madrid.
Spectrographic study of minor elements in minerals, clays, and coal ashes.
236. Louis, Marcel; Inst. Français du Pétrole, Rueil-Malmaison, France.
"Geochimie du Petrole."
237. Love, S. K., and Hastings, W. W.; U.S. Geol. Survey, Washington 25, D.C.
Chemistry of waters.
238. Lovering, T. S.; U.S. Geol. Survey, Denver 14, Colo.
Rock alteration and ore formation.
239. Low, E. M.; see Hutchinson, G. E.
240. Lowenstam, H. A.; Calif. Inst. Technol., Pasadena 4, Cal.
Isotopic composition of C and O in carbonates.
241. Lundegardh, P. H.; Univ. Uppsala, Sweden.
Geochemistry of iron ores; Geochemistry of Cr, Co, Ni, and Zn; Minor elements in igneous rocks.
242. McConnell, Duncan; Ohio State Univ., Columbus, Ohio.
Crystal chemistry of phosphates.
243. MacDonald, Gordon; Hawaii Volcano Observatory, Hawaii National Park, Terr. Hawaii.
Petrology of basaltic rocks; Volcanology.
244. McKelvey, V. E. (and Bulbrandsen, R. A. and Swanson, R. A.); U.S. Geol. Survey, Melo Park, Cal.
Geochemistry of marine phosphates.
245. McKinstry, H. E.; Harvard Univ., Cambridge 38, Mass.
Ore deposits.

246. McKnight, E. T.; U.S. Geol. Survey, Washington 25, D.C.
Ore deposits of the Tri-State District.

247. Machatschki, Felix; Mineral. Inst., Univ. Vienna.
"Spurenelmenteverteilung im Bereiche der verschiedenen metasomatischen Blei-Zink Erzlagerstatten in Osterreich."

248. Marble, J. P.; U.S. Natl. Museum, Washington 25, D.C.
"Age determinations by lead-uranium-thorium analyses; Preparation of annual report of Committee on Measurement of Geologic Time, National Research Council."

249. Marsal, Dietrich; Bayerisches Geol. Landesant, Munich, Germany.

250. Marshall, C. E.; Univ. Missouri, Columbia, Mo.
"Colliod chemistry of silicates; Minor elements in soils and clays."

251. Mason, Brian; American Museum Natural History, New York 24, N.Y.
(and Taylor, S. R.)
"Minor elements in New Zealand rocks."

252. May, I. H.; see Grimaldi, F. S.

253. Maxwell, J. A.; Geol. Survey Canada, Ottawa.
Geochemistry of chert.

254. Mertie, J. B., Jr.; U.S. Geol. Survey, Washington 25, D.C.
Monazite in granitic rocks of southeastern U.S.

255. Merwin, H. E.; see Zies, E. G.

255b. Metrot, R.; Soc. Cherifienne de Pétroles, Rabat, Morocco.
Oil geochemistry.

256. Meyer, Charles; Univ. California, Berkeley, Cal.
Rock alteration associated with ore deposits.

257. Michel-Levy, M.; 26 Rue Spontini, Paris.
Hydrothermal synthesis of minerals.

258. Michot, Paul; Lab. Petr. and Géochim., Univ. Liège, Belgium.
"Geochemical relations of anorthosite."

259. Miholic, Stanko; 10 Svibovac, Zagreb, Yugoslavia.
"Geologic age determinations from radioactive decay of samarium into neodymium; Relative age of sedimentary rocks determined from the trace elements contained in them."

260. Millot, Georges; Lab. de Géochim., Univ. Nancy, France.
"Géochimie des argiles et des phyllitvs; Le cycle des silicates."

261. Milton, Charles; U.S. Geol. Survey, Washington 25, D.C.
"Mineralogy of ores; Igneous and metamorphic petrology."

262. Minami, Eiichi; Univ. Tokyo, Japan.
"Geochemistry of fluorine in Japanese hot springs, mineral springs, in natural calcium carbonates, especially calc-sinters of hot springs, in igneous rocks, and in sedimentary rocks; Radiochemical investigation of Japanese meteorites."

263. Minguzzi, Carlo; Inst. Mineral Petrog. Univ, Pavia, Italy.
"Distribution of elements in the ophiolitic association of the Appenines and their redistribution through weathering; Distribution of trace elements in petroleum from the Po Valley."

264. Mitchell, R. J. and Swaine, D. J.; Macaulay Inst. Soil Research, Craigiebuckler, Aberdeen, Scotland.
Minor elements in soils and plants. See Wager, L. R.

265. Morey, G. W.; Geophysical Lab., 2801 Upton St., N.W., Washington, D.C.
Equilibrium in systems containing H_2O.

266. Morita, Yoshimi; Univ. Nagoya, Japan.
Copper and zinc in waters.

267. Müller, Wolfgang; see Pietsch, E. H.

267b. Muir, Alex; Rothamsted Experimental Station, Harpenden, Herts.
Rocks weathering; Soil chemistry.

268. Mukherjee, B.; see Dutta, R. K.

269. Murakami, Yukio; Chem. Inst., Univ. Tokyo, Japan.
Thallium in minerals and ores.

270. Murata, K. J.; U.S. Geol. Survey, Washington 25, D.C.
"Spectrographic determination of minor elements in rocks and minerals; Minor elements in Paricutin lavas; (and Rose, H. J. and Carron, M. K.) Determination of rare earths in minerals."

271. Myers, A. T.; U.S. Geol. Survey, Denver 14, Colorado.
"Spectrographic determination of minor elements; (and Canney, F. C.) Development of mobile spectrographic laboratory."

272. Naeser, C. R.; U.S. Geol. Survey, Washington 25, D.C.
"Chemistry of rare earths."

273. Nagelschmidt, Gunther; Sheffield, England.
"Safety in Mines Research"
"Biochemistry of silicon."

274. Naughton, J. J.; Dept. Chem., Univ. Hawaii, Honolulu 14, Terr. Hawaii.
"Relative abundances of isotopes of C and H in volcanic effluvia; Radioactivity of Hawaiian lavas."

275. Neuerburg, G. J.; U.S. Geol. Survey, 12615 Chandler Blvd., North Hollywood, California.
"Uranium in igneous rocks; Minor elements as clues to the chemical history of igneous rocks."

276. Neumann, Henrich; Mineral Museum, Univ. Oslo, Norway.
"Distribution coefficients of trace elements in minerals."

277. Newhouse, W. H.; Univ. Chicago, Chicago 37, Illinois.
Migration of elements in metamorphic processes.

278. Nicolaysen, L. O.; see Walker, F.

279. Nier, A. O. C.; Univ. Minnesota, Minneapolis, Minnesota.
"Measurement of the abundances of the lead isotopes; Isotope analyses of minute amounts of rare gases (He^3, A); Determination of trace elements in solids by mass spectrometry."

280. Nieuwenkamp, W.; Inst. Mineral. Geol., Univ. Utrecht, Netherlands.
"Chromium content of amphibolites and allied rocks."

281. Noble, J. A.; Calif. Inst. Technol., Pasadena 4, California.
Minor elements in ore minerals.

282. Nockolds, S. R.; Dept. Mineral. Petrol., Cambridge Univ., England.
"Geochemistry of trace elements in igneous rocks." See Walker, F.

283. Noddack, Ida and Noddack, Walter; Geochem. Inst., Bamberg, Germany.
"Häufigkeit und Verteilung der chemischen Elemente in der Meteoriten, in der Erde, und in Organismen; Entwicklung and Verbesserung der Methoden zum Nachweis der chemischen Elemente; Geochemische Altersbestimmungen; Zeitliche Veränderungen an Mineralien; Geochemische und Geophysikalische Methoden zur Lagerstättensuche."

284. Norton, D. R.; U.S. Geol. Survey, Washington 25, D.C.
Minor elements in oceanic waters.

285. Oana, Sinya; Lab. of Geochem., Univ. Nagoya, Japan.
"Geochemical prospecting for natural gases; Argon in natural waters."

286. Odum, H. T.; Dept. Biol., Univ. Florida, Gainesville, Florida.
"Biochemistry of strontium; Phosphorus in fresh and marine waters of Florida."

287. Oftedal, Ivar; Mineral Inst. Univ., Oslo, Norway.
Spectrochemical analyses.

288. Onishi, Hiroshi; see Sandell, E. B.

289. Orcel, Jean; Lab. Mineral., Museum d'Hist. Nat., Paris, France.
"La minéralogie et la géochimie des élements radioactifs."

290. Osborn, E. F. and Roy, Rustum; Pennsylvania State Univ. State College, Pennsylvania.
"Phase equilibria in silicate systems; Phase equilibria and stability relations in systems with water."

291. Otte, V.; see Borchert, H.

292. Page, L. R.; U.S. Geol. Survey, Denver 14, Colorado.
Geochemical associations of uranium.
293. Paneth, F. A.; Lab. for Radiochem., Max. Planck-Institute, Mainz, Germany.
"Composition of the stratosphere; Age determinations of meteorites and minerals."
294. Park, C. F.; Stanford Univ., Palo Alto, California.
Ore deposits.
295. Patterson, C. C.; see Brown, H. S.
296. Patterson, E. M.; Dept. Geol. Mineral., Univ. St. Andrews, Scotland.
"Petrochemistry of Tertiary extrusive rock in northeastern Ireland and western Scotland."
297. Pearce, D. W.; 1814 Hunt Street, Richland, Washington.
Chemistry of rare earths.
298. Peck, L. C.; U.S. Geol. Survey, Denver 14, Colorado.
Chemical analysis of rocks and minerals.
299. Pecora, W. T.; U.S. Geol. Survey, Washington 25, D.C.
"Petrology of alkalic rocks; Carbonatites."
300. Peoples, J. W.; Wesleyan Univ., Middletown, Connecticut.
"Differentiation of lava flows of the Connecticut Valley."
301. Permingeat, Francois; Service Géol., Rabet, Morocco.
Mineral chemistry.
302. Pettersson, Hans; Oceanograph Inst., Göteborg, Sweden.
Deep sea sediments.
303. Phair, George; U.S. Geol. Survey, Denver 14, Colorado.
Uranium in igneous rocks.
304. Phillips, F. C.; Univ. Bristol, England.
"Distribution of uranium and thorium in rocks; Isotope ratios in waters of hot springs at Bath, Hotwells, etc."
305. Phillips, R.; Univ. Durham, England.
"The system of FeO-Fe_2O_3-TiO_2." See Dunham, K. C.
306. Picciotto, E. E.; Lab. Phys. Nucleaire, Univ. Libre de Bruxelles, Belgium.
"Géochimie des éléments radioactifs dans les sédiments océaniques; Localisation des mineraux radioactifs dans les roches."
307. Pieruccini, Renzo; Univ. Messina, Italy.
Spectrographic determination of minor elements in sedimentary rocks.
308. Pietsch, Erich, Müller, Wolfgang and Kubach, Ilsa; Gmelin Inst. Clausthal-Zellerfeld, Germany.
"Geochemie in Rahmen des Gmelin-Handbuches."
309. Pinson, W. H.; Harvard Univ., Cambridge 38, Massachusetts.
Spectrographic determination of minor elements in rocks and in meteorites.
310. Pitcher, W. S.; Dept. Geol., Imperial College, London, England.
"Trace elements in metamorphic and granitic rocks; Geochemical prospecting."
311. Polanski, Anthony; Zaklad Mineral. Petrograf., Univ. Poznan, Poland.
312. Poldervaart, Arie; Columbia Univ., New York 27, N.Y.
Metamorphism of igneous rocks; Relative amounts of rock types.
313. Poole, J. H. J.; Trinity College, Dublin, Ireland.
Evolution of the Earth's atmosphere.
314. Powers, H. A.; U.S. Geol. Survey, Denver 14, Colorado.
Volcanism and volcanic rocks.
315. Preuss, E.; Univ. München, Germany.
Minor elements in ores and minerals.
315b. Pridee, R. T.; Univ. of W. Australia, Perth.
"Radioactive age determinations; Geochemical relations of anorthosite; Petrology of alkaline rocks."
316. Pruvot, P.; Rue Jean Lavaud, Fontenay aux Roses (Seine), France.
"Spectrophotometrie de flammes dans l'analyse des silicates."

317. Quervain, F. de; Schweiz Geotechn. Kommission, Zürich, Switzerland.
"Samenstelle von mineral—und gesteinchemischen Daten."
318. Quiring, Heinrich; Techn. Univ. Berlin, Germany.
Origin of ores.
319. Rabbitt, J. C.; U.S. Geol. Survey, Washington 25, D.C.
"Geochemistry of uranium."
320. Rader, L. S.; U.S. Geol. Survey, Denver 14, Colorado.
See Grimaldi, F. S.
321. Rafter, T. A.; Dominion Lab., Wellington, New Zealand.
"Radiocarbon dating; Isotopic ratios of sulphur in New Zealand colas."
322. Raguin, E.; École Supérieure des Mines, Sceaux, Seine, France.
323. Rakestraw, N. W.; Scripps Inst. Oceanography, La Jolla, California.
Chemistry of sea water.
324. Ramberg, Hans; Dept. Geol., Univ. Chicago 37, Illinois.
"Stability of minerals from thermochemical considerations; Crystal chemistry and energies; Distribution of elements among co-existing minerals."
325. Ramdohr, Paul; Mineralog. Inst., Univ. Heidleberg, Germany.
"Mineralogy and paragenesis of ores."
326. Rankama, Kalervo; Geol. Dept., Univ. Helsinki, Finland.
"Geological applications of the nuclides, both stable and radioactive; Origin of carbon in ancient carbonaceous schists in Manitoba, by means of stable carbon isotopes; Chemistry and origin of tektites (with O. Joensuu); Abundance of the elements in igneous rocks."
327. Read, H. H.; Dept. Geol., Imperial College, London, England.
328. Reiche, Parry; Univ. New Mexico, Albuquerque, New Mexico.
Weathering of rocks.
329. Reinhard, Max; Inst. Mineral. Petrol., Univ. Basel, Switzerland.
"Oxygen isotopes in silicate minerals and rocks; Isotopes of Ca and K in rocks."
330. Revelle, R. R.; Scripps Inst. Oceanography, La Jolla, California.
331. Reynolds, D. L.; Grant Inst. Geol., Univ. Edinburgh, Scotland.
"Trace elements in the Newry plutonic complex."
332. Reynolds, J. H.; Dept. Physics, Univ. California, Berkeley, Cal.
Isotopic composition of argon; (with J. Verhoogen) Isotopic composition of silicon.
333. Richter-Bernburg, Gerhard; Amt fur Bodenforschung, Hannover, Germany.
Ore metals in sedimentary rocks.
334. Richter, D. H.; see Ingerson, Earl.
335. Ridge, J. D.; Pennsylvania State Univ., State College, Pennsylvania.
"Geochemistry of tin."
336. Riley, Leonard; U.S. Geol. Survey, Denver 14, Colorado.
Association of minor elements with uranium and vanadium ores.
337. Ritchie, J. A.; Dominion Lab., Wellington, New Zealand.
"Investigation of rapid methods for the volumetric analysis of rocks."
338. Robinson, R. J.; Oceanographic Lab., Univ. Washington, Seattle 5, Wash.
339. Robinson, S. C.; Geol. Survey Canada, Ottawa, Canada.
Mineralogy of uranium deposits.
340. Roedder, Edwin; Dept. Mineral., Univ. Utah, Salt Lake City, Utah.
"Equilibria in silicate systems; Silicate systems with water; Composition and significance of fluid inclusions in minerals."
341. Roques, Maurice; Lab. Geol. Mineral., Clermont-Ferrand, France.
342. Rose, H. J.; see Murata, K. J.
343. Rose, Hermann; Univ. Hamburg, Germany.
Trace elements in rocks and ores.
344. Rosenqvist, I. T.; Geoteknisk Institutt, Oslo, Norway.
345. Rosholt, J. N.; U.S. Geol. Survey, Denver 14, Colorado.
Determination of uranium and thorium by radioactivity measurements.

346. Ross, C. S. and Smith, R. L.; U.S. Geol. Survey, Washington 25, D.C.
"Petrology of volcanic rocks; Welded tuffs."
346b. Roubault, M.; Dir. of Ecole géol. appliquée, Univ. Nancy, France.
Geochemistry of petrology.
347. Rowland, R. A.; Shell Oil Co., P.O. Box 2099, Houston 1, Texas.
348. Roy, Rustum; see Osborn, E. F.
349. Rubey, W. W.; U.S. Geol. Survey, Washington 25, D.C.
"Geologic history of sea water; Analyses of sedimentary rocks."
350. Russell, R. G.; Gulf Research and Development Co., Pittsburgh, Pa.
Minor elements in petroleum.
351. Sahama, T. G.; Geol. Dept., Univ. Helsinki, Finland.
"Thermochemistry of minerals."
352. Saito, Nobufusa; see Kohman, T. P.
353. Salmi, Martti; Geol. tutkimuslaitos, Helsinki, Finland.
Trace elements in peat.
354. Sandell, E. B. and Onishi, Hiroshi; Dept. Chem., Univ. Minnesota, Minneapolis, Minnesota.
"Geochemistry of arsenic."
354b. Santangelo, M.; Inst. Geofisica, Rome, Italy.
Radioactivity.
355. Saunders, D. F.; see Daniels, F.
356. Schairer, J. F.; Geological Lab., 2801 Upton Street, N.W., Washington 25, D.C.
Equilibria in silicate systems.
357. Schaller, W. T.; U.S. Geol. Survey, Washington 25, D.C.
Synthesis and conditions of stability to borate minerals; Manganese silicate minerals.
358. Schleicher, J. A.; Kansas State Geol. Survey, Lawrence, Kansas.
"Major and minor elements of limestones of eastern Kansas; Chemical and spectrochemical study of phosphatic shales."
359. Schlecht, W. G.; U.S. Geol. Survey, Washington 25, D.C.
"Precision and accuracy of rock analyses."
360. Schmitt, Harrison; Silver City, New Mexico.
Ore deposits.
361. Schneiderhöhn, Hans; Mineral. Inst., Univ. Freiburg i. Br., Germany.
Ore deposits.
362. Schoeller, Henri; Lab. Geol., Univ. Bordeaux, France.
"Chimie des eaux des gisements de petrole."
363. Schroll, Erich; Mineral. Inst., Univ. Vienna, Austria.
"Regionals geochemische Untersuchungen in den Ostalpen; Spurenelemente in Erzen; Elementverteilung in Zentral granodioritgneis des Tauernfesters."
364. Schüller, Arno; Husstr. 38, Berlin-Adlershof, Germany.
"New edition of G. Berg Vorkommen und Geochemie der mineralischen Rohstoffe."
365. Schwander, Hans; see Baertschi, P.
366. Schwartz, G. M.; Dept. Geol., Univ. Minnesota, Minneapolis, Minn.
Paragenesis of ore minerals; Alteration associated with ore deposits.
367. Senftle, F. E.; U.S. Geol. Survey, Washington 25, D.C.
Radioactivity of rocks.
368. Shand, S. J.; Fintry Place, Broughty-Ferry, Dundee, Scotland.
Chemistry of igneous rocks.
369. Shapiro, Leonard; see Brannock, W. W.
370. Shaw, D. M.; McMaster Univ., Hamilton, Ontario.
"Distribution of minor elements in metamorphic and magmatic rocks."
371. Sherman, G. D.; Hawaii Agric. Expt. Sta., Honolulu, Terr. Hawaii.
"Genesis of tropical soils; Clay minerals in soils."
372. Shika, Kiyotaki; Shinshu Univ., Nagano, Japan.
373. Shrode, R. S.; see Lamar, J. E.

374. Smales, A. A.; Atomic Energy Research Establishment, Harwell, England.
"New methods for the determination of minute quantities of the elements."
375. Smith, F. G.; Univ. Toronto, Ontario.
"Partition relations between silicate and water solutions; Development of techniques for measuring temperature-stress relations around inclusions in minerals; Determination of the composition, temperature, and pressure of the solutions responsible for deposition of vein minerals."
376. Smith, J. R.; see Hess, H. H.
377. Smith, R. L.; see Ross, C. S.
378. Smith, W. C.; U.S. Geol. Survey, Claremont, Cal.
Boron and strontium in saline deposits.
379. Smits, F.; Phys. Inst., Univ. Frieburg i. Br., Germany.
"Alterbestimmungen an Zechsteine und an Kalifeldspäten; K-A, U-He, und U-Pb Methode."
380. Sokoloff, V. P.; Johns Hopkins Univ., Baltimore, Md.
Geochemistry of soils; Geochemical prospecting.
381. Sosman, R. B.; Dept. Ceramics, Rutgers Univ., New Brunswick, N.J.
382. Spangenberg, K.; Mineral. Inst., Univ. Tübingen, Germany.
383. Stadnichenko, T. M. and Zubovic, Peter; U.S. Geol. Survey, Washington 25, D.C.
"Minor elements in coals of U.S."
384. Stern, T. W. and Stieff, L. R.; U.S. Geological Survey, Washington 25, D.C.
"Age of uranium deposits of Colorado Plateau."
385. Stevens, R. E.; U.S. Geol. Survey, Denver 14, Colo.
Methods of chemical analysis of rocks and minerals.
386. Stewart, F. H.; Dept. Geol., Univ. Durham, England.
"Petrography and chemistry of the potash-bearing evaporites of north eastern Yorkshire."
387. Stieff, L. R.; see Stern, T. W.
388. Stillwell, F. L.; Commonwealth Sci. Ind. Research Organization, Melbourne, Australia.
Paragenesis of ore minerals.
389. Straaten, L. M. J. U. van.; Geol. Inst., Univ. Groningen, Netherlands.
"Tidal flat studies."
390. Stringham, Bronson; Dept. Geol., Univ. Utah, Salt Lake City, Utah.
391. Strock, L. W.; Sylvania Corp., Bayside, N.Y.
Polymorphism.
392. Strunz, Hugo; Mineral. Inst., Tech. Hochschule, Regensburg, Germany.
Crystal chemistry.
393. Sudo, Toshio; Geol. Mineral. Inst., Univ. Tokyo.
"Clay minerals; Iron chlorites; Secondary minerals associated with Ni and Mo ore; Wall rock alterations of ore deposits; Microchemical tests of minerals."
394. Suess, H. E.; U.S. Geol. Survey, Washington 25, D.C.
"Radiocarbon dating; Cosmic abundances of elements."
395. Sugawara, Ken; Lab. Analyses and Geochemistry, Univ. Nagoya, Japan.
"Revision of abundance of Cu and Zn; Geochemical studies of Lake Biwa."
Vanadium in atmosphere.
396. Sujkowski, Z. L.; McMaster Univ., Hamilton, Ontario.
Chemical composition of sedimentary rocks.
397. Swaine, D. J.; see Mitchell, R. L.
398. Swings, P.; Univ. Liege, Belgium.
Cosmochemistry.
399. Szadeczky-Kardoss, Elémér; Lorand Eötvös. Univ., Budapest, Hungary.
Geochemical migration of elements; Crystal chemistry.
400. Talluri, Anna; Inst. Mineral., Univ. Firenze, Italy.
Minor elements in ore minerals.

401. Tanaka, Motoharu; Univ. Tokyo.
Manganese in waters.
402. Tassel, R. van; Koninkl. Natuur Museum, Brussels 4, Belgium.
403. Taylor, S. R.; Univ. Indiana, Bloomington, Ind.
See Mason, B.
404. Thayer, T. P.; U.S. Geol. Survey, Washington 25, D.C.
Relation of chemical composition of chromite to the composition of associated rocks.
405. Thode, H. G.; McMaster Univ., Hamilton, Ontario.
"Fractionation of sulphur isotopes in biological and geological processes; Spontaneous and neutron fission in radioactive minerals."
406. Thompson, J. B.; Dept. Mineral., Harvard Univ., Cambridge 38, Mass.
407. Thompson, M. E.; see Weeks, A. D.
408. Thompson, T. G.; Oceanographic Lab., Univ. Washington, Seattle 5, Wash.
"Distribution of copper in the sea and in sea sediments; Distribution of strontium in the sea; Deposition of salts on the freezing of sea water."
409. Thompson, K. B.; see Lamar, J. E.
410. Thoreau, J.; Univ. Louvain, Belgium.
"Distribution des éléments chimiques dans les pegmatites."
411. Tilley, C. E.; Dept. Mineral. Petrol., Cambridge Univ., England.
"Geochemistry of alkalic rocks formed by contamination with limestone."
412. Tilton, G. R.; see Aldrich, L. T.
413. Tomkeieff, S. I.; King's College, Univ. Durham, England.
"Chemical petrology."
413b. Tonani, F.; Inst. Geochim., Univ. Firenze, Italy.
Geochemical distribution coefficients.
414. Tongeren, W. van.; Analyt. Lab., Univ. Amsterdam, Netherlands.
"The distribution of chemical elements in their natural occurrences; Chemical analyses."
415. Trask, P.D.; 240 Southampton Ave., Berkeley 7, Cal.
Chemistry of sedimentary rocks.
416. Tripp, R. M.; Research, Inc., 1511 Levee St., Dallas 2, Texas.
"The locus of the radioelements in sediments and soils; Quantitative distribution of trace elements in the vicinity of ore bodies; Distribution of germanium in sulfide ores; Organic constituents in ancient and modern sediments and soils; Relationship between cation exchange capacity, H ion concentration, and the organic and trace element of modern sediments and soils."
417. Troeger, W. E.; Mineral Inst., Techn. Hochschule, Darmstadt, Germany.
418. Tsuboi, Seitaro; Geol. Inst., Univ. Tokyo.
"Geochemical studies of magmatic waters in cavities of nepheline basalt flows."
419. Tsuchuja, Yasuhiko; Kyushu Univ., Fukuoka, Japan.
Strontium in corals.
420. Tunell, George; Univ. California, Los Angeles 24, Cal.
Solubility of sulphide minerals.
421. Turner, F. J.; Dept. Geol. Univ. California, Berkeley, Cal.
"Facies principle in metamorphism."
422. Tuttle, O. F.; Pennyslvania State Univ., State College, Pa.
Equilibria in systems containing water; (and Keith, M. L.) Significance of variation in the properties of quartz and feldspar from common rocks.
423. Uchiyama, Aiji; see Brown, H. S.
424. Urbain, Pierre; Lab. Hydrol. et Climatol., Paris V^{e}.
"Teneurs des oligo-elements dans les eaux thermominerales, les sediments, et les roches; Les processes geochimiques d'alteration des feldspaths."
425. Urey, H. C.; Inst. for Nuclear Research, Univ. Chicago, Chicago 37, Ill.
Origin of planets and their atmospheres;
Composition of meteorites.

426. Vallentyne, J. R. and Hutchinson, G. E.; Osborn Zoological Lab., Yale Univ., New Haven, Conn.
"Nature of the nitrogenous compounds dissolved in lake water."
427. Van der Walt, C. F. J.; Geo. Survey, P.O. Box 401, Pretoria, Union S. Africa.
428. Vendl, A.; Univ. Sci. Technol., Budapest, Hungary.
429. Verhoogen, Jean; Dept. Geol., Univ. California, Berkeley.
"Kinetics of metamorphic reactions." See Reynolds, J. H.
430. Vhay, J. S.; U.S. Geol.-Survey, Spoane, Wash. Cobalt deposits.
431. Vincent, E. A.; Dept. Geol., Mineral, Oxford Univ., Oxford, England.
Chemical analysis of rocks and minerals.
432. Vincent, H. G. C.; Univ. Capetown, Union S. Africa. See Walker, F.
433. Vogt, Thorolf; Tekniske Högskule, Trondheim, Norway.
Geochemical and geobotanical ore prospecting.
434. Vuagnat, Marc; Univ. Geneva, Switzerland.
Crystal chemistry; Chemical petrology.
435. Wager, L. R.; Dept. Geol. Mineral., Oxford Univ., Oxford, England.
"Geochemistry of the minor elements of layered intrusions; (with Mitchell, R. L.) Trace elements of tertiary granites and granophyres of Scotland compared with the more acid Lewisian gneiss and Torridonian arkoses."
436. Wahl, Walter; Univ. Helsinki, Finland.
Composition of meteorites.
437. Walker, Frederick; Dept. Geol., Univ. Capetown, Union S. Africa.
(and Vincent, H. G. C.) Separation and chemical analysis of the granite and diabase of U.S. Geol. Survey Bull. 980; (and Ahrens, L. H.) Trace elements of the Palisades diabase; (and Nicolaysen, L. O.) The petrology of Mauritius; (and Nockolds, S. R.) The Petrochemistry of the Messum ring-complex, S.W. Africa."
438. Walton, M. S.; Dept. Geol., Yale Univ., New Haven, Conn.
Igneous petrology.
439. Ward, F. N.; see Lakin, H. W.
440. Waring, C. L.; see Helz, A.; Larsen, E. S., Jr.
441. Warren, H. V.; Univ. British Columbia, Vancouver.
"Biochemistry of copper in various climates; Biochemistry of molybdenum in various climates; Methods for the analysis of vegetation for Co and Ni."
442. Wasserstein, Benno; Geol. Survey, P.O. Box 401, Pretoria, Union S. Africa.
Spectroscopic determination of elements.
443. Waters, A. C.; Dept. Geol., Johns Hopkins Univ., Baltimore, Md.
"Geochemistry of Columbia River basalts and related volcanic rocks."
444. Webb, J. S.; Royal School of Mines, London.
Geochemical prospecting.
445. Wedepohl, K. H.; Mineral-Inst., Univ. Göttingen, Germany.
Geochemistry of zinc and lead.
446. Weeks, A. D. and Thompson, M. E.; U.S. Geol. Survey, Washington 25, D.C.
Mineralogy of uranium.
447. Wells, F. G.; U.S. Geol. Survey, Washington 25, D.C.
Ore deposits as related to the formation of geosynclines.
448. Wenk, E.; see Baertschi, P.
449. Wéry, A.; Inst. geol., Univ. Louvain, Belgium.
450. White, D. E. and Brannock, W. W.; U.S. Geol. Survey, Menlo Park, Cal.
Geochemistry of Steamboat Springs, Nevada.
451. White, W. S.; U.S. Geol. Survey, Calumet, Mich.
Chemistry of copper deposits of Michigan.
452. Whitehead, W. L.; Mass. Inst. Technol., Cambridge 39, Mass.
Origin of petroleum.

453. Wickman, F. E.; Riksmuseet, Stockholm 50, Sweden.
Isotopes of C and B; (and Gavelin, S. and Landergren, S.) Variation in relative abundance in the isotopes of lighter elements.
454. Wiik, H. B.; Univ. Helsinki, Finland.
Chemical analyses of rocks and meteorites.
455. Wilcox, R. E.; U.S. Geol. Survey, Denver 14, Colo.
Composition of Paricutin lavas.
456. Wildt, Rupert; Dept. Astronomy, Yale Univ., New Haven, Conn.
457. Williams, David; Dept. Geol., Imperial College, London.
"Geochemistry of the metamorphic rocks of part of Donegal and parts of northwestern Scotland; Geochemical prospecting; Distribution of trace elements in wall-rock and in economic minerals."
457b. Wilson, A. F.; Univ. of W. Australia, Perth.
Chemical relations of metasomatism. The charnochite problem. Luminescence of minerals.
458. Wilson, H. D. B.; Dept. Geol., Univ. Manitoba, Winnipeg, Manitoba.
Geochemistry of ore deposits.
459. Wilson, S. H.; Dominion Lab., Wellington, New Zealand.
"Investigation of the geothermal regions of New Zealand—development of geothermal power, analyses of gases and waters from hot springs and fumaroles."
460. Wimmenauer, Wolfhard; Geol. Landesamt Baden-Württemberg, Freiburg-i-Br., Germany.
Petrology of the Kaiserstuhl, Baden; Uranium in ores of the Wittichen area.
461. Winkler, H. G. F.; Univ. Marburg, Germany.
Growth of crystals; Course of crystallization of basaltic magma.
462. Wiseman, J. D. H.; see Bannister, F. A.
463. Wylie, A. W.; Commonwealth Sci. Ind. Research Org., Melbourne, Australia.
"Sources of the rare earths, thorium, germanium, scandium, and some other elements."
464. Yagi, Kenzo; Tohoku Univ., Sendai, Japan.
"Petrochemical aspects of igneous rocks."
465. Yamagata, Noboru; Faculty of Technology, Cumma Univ., Maebashi, Japan.
"Presence of rare alkali metals in the waters and plants in Japan."
466. Yamasaki, Kazuo; Chem. Inst., Univ. Nagoya, Japan.
"Trace elements in rocks; Distribution of Co in soils and plants in the area of cattle disease; Chemical analyses of Japanese minerals."
467. Yoder, H. S., Jr.; Geophysical Lab., 2801 Upton St., N.W., Washington, D.C.
Equilibrium studies of systems containing H_2O; Stability regions of micas.
468. Zies, E. G. and Merwin, H. E.; Geophysical Lab., 2801 Upton St., N.W., Washington, D.C.
Chemistry of volcanic rocks, ash, and sublimates from Guatamala.
469. Zubovic, Peter; see Stadnichenko, T. M.

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GEOCHEMISTRY IN JAPAN

The earliest record of geochemical investigation in Japan is traced back to a handwritten note "Geologie und Meteorologie" by PHILLIP FRANZ SIEBOLD, kept in Japan-Institut in Berlin, wherein he reports the result of examination of a number of thermal springs in Kyusyu district. The investigation was done during his stay at Nagasaki as a Dutch medical officer (1823–1829) surely by the help of his Japanese students.

Geochemical research in the modern sense started in Japan about thirty years ago by the leadership of Professor YUJI SHIBATA, now the president of Tokyo Metropolitan University and emeritus professor of Tokyo University and Nagoya University. Further this was stimulated by "La Géochimie" of VERNADSKY and the first series of GOLDSCHMIDT'S "Geochemische Verteilungsgesetze."

The first symposium on geochemistry took place in Tokyo 1941 on the occasion of the annual meeting of the Chemical Society of Japan; subsequently with one year interruption of 1945 in the postwar confusion, one or two symposia have been held yearly. At the meeting in Kyoto in

April 1953, the Geochemical Society of Japan was organized with 230 members, for the promotion of geochemical investigations in this country by facilitating an intimate contact of individual researchers and for representing Japanese Geochemistry abroad. It is headed by President Yuji Shibata and its office is located in the Institute of Earth Sciences, Faculty of Science, Nagoya University, Chikusa-ku, Nagoya.

Announcements of interest to Japanese geochemists should be addressed in duplicate to: The Office of the Society and The Science Council of Japan, Ueno Park, Tokyo, Japan.

Main Institutions in Japan where geochemical studies are being carried out are as follows. The description is done in sequence of their location from north towards south.

Hokkaido University, Sapporo.

Institute of Geology and Mineralogy.

Professor Zyunpei Harada: Chemical composition of minerals.
Professor Jun Suzuki: Igneous rocks and metamorphic rocks.

Chemical Institute.

Professor Yasumitsu Uzumasa, Assistant Professor Masakichi Nishimura: Hot springs.

Tohoku University, Sendai.

Institute of Petrology, Mineralogy, and Economic Geology.

Professor Manjiro Watanabe: Ore deposits.

Institute of Earth Sciences.

Professor Kenzo Yagi: Petrological aspects of igneous rocks.

Chemical Institute.

Professor Shin'ichro Hakomori: Micro-elements in animal and plant bodies.

Tokyo University, Tokyo.

Geological Institute.

Professor Seitaro Tsuboi: Igneous action.
Professor Takeo Watanabe: Ore deposits (particularly boron minerals).
Assistant Professor Hisashi Kuno: Chemical composition of volcanic rocks including both major and trace elements

Department of Chemistry.

Professor Kenjiro Kimura: Geochemical prospecting for metallic ore deposits. Hot springs. Distribution of rare elements in minerals of Japan (including radioactive elements, rare earth elements, germanium, etc.).
Professor Eiichi Minami, Assistant Professor Nobufusa Saito: Japanese hot springs, sinters and other deposits. Fluorine in hot springs, sediments and igneous rocks. Japanese meteorites.

Tokyo Educational University (Tokyo Kyoiku Daigaku), Otsuka-kubomachi, Bunkyo-ku, Tokyo.

Geological Institute.

Professor Toshio Sudo: Clay mineralogy.
Professor Hidetaka Shibata: Pegmatites.

Chemical Institute.

Professor Hiroshi Hamaguchi: Sea salt and marine sediments.

Tokyo Institute of Technology (Tokyo Kogyo Daigaku), Meguro-ku, Tokyo.

Laboratory of Analytical and Geochemistry.

Professor Iwaji Iwasaki: Volcanoes, hot springs and other natural waters.

Tokyo Metropolitan University (Tokyo Toritsu Daigaku), Meguro-ku, Tokyo.

Chemical Institute.

Professor Kimio Noguchi, Assistant Professor Takahisa Hanya: Inland waters, volcanic gases and statistics.

Meteorological Research Institute, Mabashi Sugunami-ku, Tokyo.

Geochemical Laboratory.

Yasuo Miyake (Chief): Oceanochemistry and meteorological chemistry.

Geological Survey of Japan, Hisamotocho, Kawasaki City, Kanagawa Pref.

Division of Geology.

Yoshinori Kawano: Chemical analyses of igneous rocks.

Nagoya University, Nagoya.

Chemical Institute.

Professor Ken Sugawara, Assistant Professor Tadashiro Koyama: Natural waters (lake, river, sea and precipitation) and related problems. Sediments metabolism.

Professor Kazuo Yamasaki: Spectrochemical analysis of trace elements in Japanese rocks and minerals.

Institute of Earth Sciences.

Professor Shinya Oana: Ground water. Argon in natural waters. Volcanic gases.

Kyoto University, Kyoto.

Chemistry Institute.

Professors Masayoshi Ishibashi: Sea salt and marine sediments.

Ohara Institute of Agricultural Research, Kurashiki City, Okayama Pref.

Jun Kobayashi: Japanese river waters.

Kyusyu University, Fukuoka.

Institute of Geology and Mineralogy.

Professor Toru Tomita: Zircon in granites. Volcanic rocks.

Assistant Professor Sadakatu Taneda: Chemical composition of Japanese volcanic rocks.

Chemical Institute.

Professor Sinnosuké Matuura, Assistant Professor Tomitaro Ishimori: Hot springs. Rare elements.

Note: This list was submitted on behalf of the Geochemical Society of Japan through Professor Ken Sugawara, who remarks "that many additional young Japanese scientists are actively engaged in geochemical studies. Some of them are attached to the enlisted centres and others are to other institutions or to some local smaller colleges. To cover the names of these scientists demands much more pages than probably you are going to allot. Of course we are ready to provide you with a more comprehensive report on your demand."

GEOCHEMISTS OF THE U.S.S.R.

As noted in the list of persons engaged in research of interest to geochemists, no replies to questionnaires were received from the U.S.S.R. A list of scientists publishing geochemical papers in the U.S.S.R. was prepared, but information as to addresses was lacking. The list was therefore sent by Professor S. I. Tomkeieff to D. S. Korzhinsky on February 1, 1954, and Dr. Korzhinsky has now advised that persons on the list may best be reached by addressing them at—

Section of Geological-Geographical Sciences
Academy of Sciences
Staromonetny 35
Moscow, U.S.S.R.

The list is therefore published in the hope that it may help in restoring communication among scientists engaged in similar research.

Michael Fleischer, President
Section of Geochemistry
International Union of Pure and
Applied Chemistry

Afanes'ev, G. D.
Agafoshin, N. P.
Alekin, O. A.
Aleksandrov, G. P.
Anosov, F. Y.
Antipov-Karataev, I. N.
Betekhtin, A. G.
Bibikova, V. I.
Borovik, S. A.
Borovik-Romanova, T. F.
Borovskii, I. B.
Brouevich, S. V.
Chirvinskii, P. N.
Chukhrov, F. V.
Danilova, V. V.
Dobryanskii, A. F.
Ginzburg, I. I.
Glebovich, T. A.
Golobolov, A. D.
Grigoriev, G. P.
Gulyaeva, L. A.
Itkina, E. S.
Kalinin, S. K.
Kapustinskii, A. F.
Karasik, M. A.
Katchenkov, S. M.
Kazmina, T. I.
Korzhinskii, D. S.
Krotov, B. P.
Kunasheva, K. G.
Kudrin, S. A.
Levedev, P. I.
Lepeshkov, I. N.
Levchenko, V. M.
Maksimovich, G. A.
Malyuga, D. P.
Menyailov, A. A.
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June 9, 1954

Book review

Geochemistry, by the late V. M. GOLDSCHMIDT. Edited by ALEX MUIR. 730 pp. (£3-3-0). Clarendon Press, Oxford 1954.

To no other individual do we owe so much for the development of geochemistry to its present state than the late V. M. GOLDSCHMIDT. His untimely death in March 1947 prevented the completion of a much awaited book which in the form of a treatise was being written after a whole lifetime's activity in geochemistry. What was written, however, has not been lost and we are greatly indebted to the editorial efforts of ALEX MUIR and those who helped him for finally bringing the manuscript into publishable form. This was by no means a small task as some of the first part had yet to be written while much of the rest was at various stages of completion.

Although GOLDSCHMIDT had been active in many aspects of geochemistry he is quick to point out the difficulties of a single author in attempting to cover all of geochemistry in detail, and he broadly defines the object of his book as "an attempt to give at least some idea of the scope of modern geochemistry." For this purpose the book has been divided into two parts, (1) General Principles of Geochemistry, and (2) Discussions of the Geochemistry of Individual Elements. In substance it probably comes closer to RANKAMA and SAHAMA's "Geochemistry" than to MASON's "Principles of Geochemistry." Unlike the former, however, it does not attempt to provide an exhaustive review of literature; the bibliography is nevertheless entirely adequate for the purpose (some 650 entries in all) and includes some Russian references which are omitted from the earlier work of RANKAMA and SAHAMA. The absence of any reference (pp. 562–567) to the fairly extensive literature on the geochemistry of uranium is, however, an unfortunate omission.

Most of the book was written in the early 1940's but has been brought up to date by editorial reference insertions, sometimes with useful paragraph-length discussions. Whereas most such insertions blend satisfactorily with what had already been written, some difficulties are unavoidable and understandable. For example, the opening sentence on the geochemistry of indium reads "The geochemistry of indium is not very well known" whereas the last sentence is an insertion which merely states that "the geochemistry of indium has been dealt with in detail by D. M. SHAW, 1952." An expansion of this statement pointing out that this recent work had indeed provided a lot of the much needed information about the geochemistry of indium would have been helpful.

Bearing in mind the extent of the geochemical investigations which GOLDSCHMIDT undertook in his lifetime, it is hardly surprising that considerable information remained unpublished when he died. The Editor has sought to incorporate this information and data such as that on the silver content of igneous rocks (Table LIV) and of sediments (Table LV) which add considerably to the value of the book.

In a discussion on the abundance of phosphorus in meteorites and igneous rocks, much needed attention is rightly drawn to two general items which require consideration and which are often overlooked when abundance calculations are made and compared; first, the accuracy of the determinations, and as an example the poor accuracy of phosphorus determinations which was recently revealed by the study of FAIRBAIRN and collaborators (U.S. Geol. Survey Bulletin 980) is cited, and second, the statistical nature of the distribution of the concentration of an element in specific rocks and minerals. Attention is drawn to the fact (Table LXXIV) that the mean phosphorus content of different igneous rocks is always greater (usually $\times 2$–3) than the mode (the most frequent observation) in a frequency distribution diagram and GOLDSCHMIDT raises the interesting question as to which of these two quantities should be used when comparing the phosphorus contents of different igneous rocks. Such a relationship between mode and arithmetic mean suggests that the distribution of the phosphorus content is probably of the lognormal type, as has been found to be the case for several other elements.

Discussions of the crystal chemical behaviour of elements and of crystal-chemistry in general are found scattered throughout the book and are a valuable feature. Much of modern crystal chemistry had its roots in GOLDSCHMIDT and his collaborators' Geochemische Verteilungsgesetze der Elemente, I—IX (Skrifter Norske Vid.-Akad., Oslo 1923–1937) and it is not surprising

therefore that many of the crystal chemical discussions are particularly satisfactory. A few crystal chemical problems which are discussed at some length, as for example, the ubiquity of silver in galena crystals (p. 408), might possibly be resolved by using some other ionic radii.

Although most of GOLDSCHMIDT's ideas have appeared in various journals and books, there remained much in his active mind which had not before been committed to print and which in one way or another appears for the first time in various parts of this book. The reviewer was particularly interested to read (pp. 100–106) for example, a discussion of the significance of ionization potentials along lines very similar to those described by him (*Geochim. et Cosmochim. Acta* **3,** pp. 1–29, 1953).

Presentation is readable and clear and has undoubtedly benefited from the assistance which GOLDSCHMIDT acknowledges in his preface. Bibliography and author index are arranged so that both may be scanned at the same time. There is a general index together with an index to rock and mineral names; each is adequate.

The book is highly recommended and should appeal to a wide audience and the price of £3-3-0 is not excessive when compared with similar books.

L. H. AHRENS.

Bemerkung zu der Arbeit von S. J. THOMSON und G. WARDLE: "Coloured natural rocksalt: a study of their helium contents, colours and impurities," *Geochim. et Cosmochim. Acta* (1954), **5,** 169.

Mit der genannten Arbeit haben die Autoren, insbesondere durch die Vermehrungen der Heliumbestimmungen, einen wesentlichen Beitrag zur Kenntnis des natürlichen strahlungsgefärbten Steinsalzes geliefert. Leider ist dabei ein Versehen unterlaufen.

Die Proben gelben Steinsalzes, Tabelle 1, p. 175, Nr. 15 und 16, sind nicht vom Grimbergschacht (Heringen) sondern von Hallstatt; sie stammen aus der Sammlung des Wiener Instituts für Radiumforschung und wurden von mir Herrn Prof. PANETH zum Zwecke der Heliumbestimmung übersandt.

Der von den genannten Autoren gefundene hohe Heliumgehalt dieses Salzes bestätigt eine Vermutung, die ich in meinem Buche "*Verfärbung und Lumineszenz*," Springer-Verlag, Wien, 1953, p. 136/137, ausgesprochen habe, doch muss noch dahingestellt bleiben, ob dieser hohe Heliumgehalt wirklich zur Erklärung der sehr labilen Gelbfärbung genügt.

K. PRZIBRAM.

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1. Papers on Geochemistry should be submitted to the editors for the appropriate country or language (*Papers on Cosmochemistry should be sent to Prof. F. A. Paneth, F.R.S.*). Papers submitted for publication will naturally be judged from the standpoint of scientific originality and novelty. Technical details of apparatus used in scientific investigation can, however, be presented in brief notes. The preparation of progress reports and review articles will be invited by the Editors from time to time. The Journal will appear as independent and complete numbers, which will be sold separately and combined into volumes of about 300 pages.

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6. To conserve space authors are requested to mark less important portions of the paper (such as description of methods, record of experimental results, etc.) for printing in smaller type.

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ISOTOPE GEOLOGY

By KALERVO RANKAMA, Ph.D.

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FORMERLY RESEARCH ASSOCIATE IN GEOCHEMISTRY AT THE UNIVERSITY OF CHICAGO

ISOTOPE geology is a term coined by the author to cover the geological applications of isotope research. In this term, the word "geology" is used in its broadest sense, and includes such branches of research as geochemistry, biology, oceanography, and hydrology. Isotope geology is a relatively new field of research, in a state of constant and rapid expansion. It already covers such domains as the determination of the absolute geological age of ancient minerals and rocks, measurement of paleotemperatures, investigation of the chemistry of the Earth during the early stages of its evolution, making of the atomic calendar for the determination of the age of Pleistocene remains and formations, etc. Many geologists already realize the vast possibilities offered by the application of isotope research to geological problems, and intensive research in this field is being carried out in a number of countries.

So far, no book has been written in any language covering the field of isotope geology, although pertinent information is scattered in papers appearing in scientific periodicals in the fields of physics, chemistry, astronomy, geology, oceanography, biology, and archaeology. This book, has been written primarily to acquaint the geologist with isotope geology and its possibilities. It also contains information of interest to physicists, chemists, and biologists who want to refer to the occurrence of the isotopes in Nature.

General content of the book. The book is divided into two parts. Part I is a review of the physics and chemistry of nuclides. Part II deals with the natural science of nuclides, i.e. their manner of occurrence in Nature. An extensive bibliography appears at the end of the book, followed by a name index and a comprehensive subject index

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